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Investigations of Interactions and Miscibility in Polyacetal/Poly(Vinyl Phenol) Blends and Applications to Compatibilized Blends Containing CARILON® Polymer

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CONTENTS

ABSTRACT

Chemical analogs of polyacetal and poly(vinyl phenol) mix exothermically as a result of favorable hydrogen bonding equilibria. Melt-compounded polyacetal/poly(vinyl phenol) blends also exhibit these favorable interactions leading to complete miscibility in the melt and in the amorphous phase. The interactions are sufficiently strong to promote miscibility between polyacetal and styrene-vinyl phenol random copolymers which contain a majority of styrene (which is non-interacting). Poly(vinyl phenol) and styrene-vinyl phenol copolymers are also miscible with polyketones, such as CARILON® polymer. Poly(vinyl phenol) was shown to be somewhat effective towards improving the compatibility of immiscible blends containing CARILON polymer and Celcon polyacetal.

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by

J. M. Machado

INTRODUCTION AND SUMMARY

The information contained in this record is part of a broad research program aimed at developing useful and compatible blends containing CARILON polymer. Part of this work involved identifying favorable interactions involving ketone groups which may drive miscibility or compatibility in polyketone blends. This was done by performing calorimetry-of-mixing measurements on model compounds or chemical analogs of the contemplated polymers.[1]

In performing this work, it was found that phenol groups interact very favorably with acetal functionalities. This led to the notion that polyacetal, an important engineering thermoplastic likely to be competitive with CARILON polymer, would be miscible with poly(vinyl phenol), a polymer which D. L. Handlin showed is also miscible with polyketone.[2]

This record contains four appendices which chronicle this work. The first is a paper published in *Polymer* which describes and quantifies the strength of hydrogen bonding interaction between polyacetal and poly(vinyl phenol) chemical analogs and applies the binary interaction model to predict the phase behavior of homopolymer and copolymer blends. The second appendix is a paper, also published in *Polymer*, which demonstrates that melt-compounded polyacetal/poly(vinyl phenol) blends are miscible in the melt and in the amorphous phase of the solid. Other aspects of this blend system are further described. The third appendix is a paper accepted in *Polymer Communications* which demonstrates that polyacetal is miscible with a styrene-vinyl phenol copolymer in accordance with predictions based on the binary interaction model. The fourth appendix is a WRC MRS published in May 1991 which demonstrates the application of the known phase behavior of blends containing polyketone, polyacetal, and poly(vinyl phenol) to produce compatibilized polyketone/polyacetal blends having enhanced tensile strength. The work described above has also led to a number of patent applications in this area.

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2. Handlin, D. L., U.S. Patent 4,812,522.

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Appendix I

Miscible Polyacetal – Poly(Vinyl Phenol) Blends: 1. Predictions Based on Low Molecular Weight Analogs

WRC 2436

MISCIBLE POLYACETAL - POLY(VINYL PHENOL) BLENDS: 1. PREDICTIONS BASED ON LOW MOLECULAR WEIGHT ANALOGS

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ABSTRACT

A chemical analog of poly(vinyl phenol) mixes exothermically with analogs of polyacetal and poly(ethylene oxide), suggesting miscibility in the case of blends of poly(vinyl phenol) with polyacetal and with poly(ethylene oxide). The interaction parameter corresponding to the poly(vinyl phenol) and the poly(ethylene oxide) analog mixtures agrees well with an interaction parameter reported for the polymer mixtures, which was based on the melting point depression of poly(ethylene oxide) in blends with poly(vinyl phenol). FTIR spectroscopy indicates the presence of strong hydrogen bonding between phenol and ether groups in these analog mixtures.

Application of the binary interaction model predicts that a rather wide range of styrene-vinyl phenol copolymers would exhibit miscibility with polyacetal.

INTRODUCTION

Since the combinatorial entropy of mixing high molecular weight polymers is small, miscibility between high molecular weight polymers usually requires exothermic mixing.[1] Direct measurements of the heat-of-mixing of polymers are generally not practical.[1 2] However, Paul et al. and Walsh et al.[1 2] have shown that the heats-of-mixing of low molecular weight model compounds is closely related to the heat effect on mixing polymers which contain the same functional groups. Paul et al.[3] have used the interaction parameters derived from low molecular weight chemical analogs in a binary interaction model to predict heat effects in the corresponding polymer blends.

Analog calorimetry and the binary interaction model have been primarily applied to blends where interactions are not very strong or directionally specific. When hydrogen-bonding or electron donor/acceptor interactions exist, mixing thermodynamics may not be well described by a mean field approach which considers only enthalpic contributions. Such interactions undoubtedly create excess entropic effects. It is also questionable whether strong interactions in analog mixtures are quantitatively similar to those in polymer blends. A recent study of blends of PMMA with copolymers of styrene and acrylic acid identified differences in the degree of hydrogen bonding among analogs and polymers.[4 5]

Two approaches are available to represent the thermodynamics of strongly interacting blends. Coleman and Painter have developed an association model for blends of polymers that hydrogen-bond.[6 7 8] Sanchez and Balasz have incorporated directionally specific interactions into a compressible lattice model.[9] Both models recognize entropic, as well as, enthalpic effects.

We are interested in defining the capabilities of analog calorimetry and the binary interaction model for predicting the phase behavior of blends which exhibit strong interactions. The poly(vinyl phenol) / polyacetal system has been chosen as a test case.

Belfiore et al recently reported miscibility in blends containing PVP and another polyether, PEO.[10] Analysis of melting point depression indicated a large exothermic interaction. FTIR identified a high level of hydrogen-bonding as the driving force for miscibility.

As the first member of the polyether family, polyacetal contains the highest fraction of electron donor sites, and has the potential to interact strongly with PVP. However, polyacetal is highly crystalline, has a high melting point, and is resistant to most solvents. This suggests a high degree of self-association which must be overcome to form miscible blends. No miscible blends involving polyacetal have been reported. In contrast, PVP is miscible with a variety of oxygen- containing polymers.[11] In copolymers with styrene only a few percent of vinyl phenol groups are required to achieve miscibility[12] with, for example, PMMA.

In this paper, we have applied analog calorimetry and the binary interaction model to predict miscibility between polyacetal and PVP and between polyacetal and copolymers of styrene and vinyl phenol. The

approach of Coleman and Painter is also used to model polyacetal - PVP. Interaction parameters derived from analog heats and reported from melting point depression analysis in polymer blends are compared for the PEO/PVP system. FTIR spectroscopy of the analog solutions indicates the presence of strong hydrogen bonding between phenol and ether analogs.

In the second paper of this series, we will present experimental evidence of miscibility between polyacetal and PVP based on thermomechanical properties of blends and compare interaction parameters derived from polymers with those derived from their analogs. The third paper of this series discusses blends of polyacetal with a copolymer of styrene and vinyl phenol.

EXPERIMENTAL

Calorimetry

The analogs used were obtained from Aldrich and are given in Table 1. All chemicals were used as received. Heats-of-mixing at 25°C for each system at several compositions were measured in a flow calorimeter from Hart Scientific.

Dimethoxymethane and ethyl benzene are both liquids at room temperature and heats-of-mixing were measured directly. The heats were fit to the van Laar expression to generate binary interaction parameters

$$\Delta H/V = B_{12}*\phi_1*\phi_2 \qquad (1)$$

where ϕ_1 and ϕ_2 are volume fractions.

Since 4-ethyl phenol is a solid at room temperature, highly concentrated solutions of 4EP in the other analogs were prepared. The heats-of-mixing these solutions against the pure liquid second analog were measured. From these dilution experiments an apparent interaction parameter was calculated:

$$B_{app} = \Delta H/(V*\phi_A*\phi_B) \qquad (2)$$

where solution B comprises analog 1 in analog 2 at composition ϕ_1. Solution A is pure analog 2. By assuming a parabolic shape to the heat-of-mixing curve we calculate B_{12} from B_{app}:

$$B_{12} = B_{app}/\phi_1^2 \qquad (3)$$

The B_{12} values are given in Table 2. The heats-of-mixing are represented as a function of volume fraction in Figure 1.

FTIR Spectroscopy

Solutions of 4EP in CCl_4 at the concentrations of 0.01M, 0.1M, and 1M were prepared for IR measurements to study the free OH stretching frequency. The hydrogen bond interactions between 4EP and the analogs of polyacetal and PEO, DMM and TEGDME, were investigated by taking the IR spectra of the 4EP/ether mixtures in CCl_4. To ensure that the hydrogen

bonding between 4EP and DMM (or TEGDME) is the dominant intermolecular interaction in the 4EP/ether mixtures, we selected 0.01M as the concentration for 4EP. The concentrations of the ethers in the mixtures were 0.1M, 0.5M, and 1M. The IR spectra of DMM and TEGDME were measured in CCl_4 at the concentrations of 0.1M and 1M to locate the overtone/combination bands of these ethers in the 3700-3000 cm^{-1} region. Identifying these overtone/combination bands allows us to unambiguously assign the H-bonded OH bands.

The IR spectra were obtained on a Nicolet 20DXB FTIR sepctrometer with a spectral resolution of 2 cm^{-1} and 100 scans co-addition. The path length of the IR cell is 0.5 mm for all spectra with the exception of 1M 4EP for which a 0.025 mm fixed path cell was used.

RESULTS AND DISCUSSION

Analog Calorimetry

The enthalpy of mixing versus composition curve, shown in figure 1, exhibits an approximately parabolic shape as required by the van Laar treatment. The maximum in the EGDME/4EP curve is shifted from the midpoint composition. For this system, the B_{12} values calculated from equation 3 exhibit a slight concentration dependence. The average value is reported in Table 2.

The endothermic heats for DMM/EB and 4EP/EB indicate that blends of PS with PAc and with PVP would be immiscible. The B_{12} value characterizing the interaction between EB and 4EP is rather large and positive. This suggests that miscibility windows in blends involving styrene - vinyl phenol random copolymers arise in part from the unfavorable interaction between these monomer units.

The large exothermic heats between 4EP and the two ethers (DMM and EGDME) suggest a strong driving force for miscibility between PVP and both PAc and PEO. FTIR spectroscopy, as described below, identifies hydrogen bonds between the phenolic hydroxyl group of PVP and the ether oxygens of PAc and PEO as the origin of this favorable interaction. However, the B_{12} values are not entirely determined by the extent of hydrogen bonding between the ethers and phenol. Mixing involves a change from two pure components to a homogeneous combination of the two. The enthalpy change reflects the difference in enthalpy of the mixture from the average of the two components. Therefore, the strength of interaction in the mix must be viewed relative to the interactions between the like molecules which it replaces.

The B_{12} values can be converted to Flory-Huggins χ interaction parameters if we assume a reference volume:

$$\chi_{12} = B_{12}Vref/(RT) \qquad (4)$$

To maintain consistency with the χ parameter reported previously for PEO/PVP, Vref is set equal to the repeat unit molar volume of PVP (=100.0cm^3).[9] For PVP/PAc we estimate χ values of -1.3 and -0.9 at 25 and 170°C respectively. The latter temperature is approximately the melting point of polyacetal. For PVP/PEO we calculate χ values of -1.7 and -1.4 at 25 and 60°C respectively. Belfiore reports χ = -1.5 based on

analysis of the melting point depression of PEO in blends with PVP over the range 70 to 50°C. This is in excellent agreement with the χ value which was derived from the analog heats.

FTIR Spectroscopy

Figure 2 shows the IR spectra of 4EP in CCl_4 at various concentrations. The stretching frequency of the free -OH group at 3614 cm^{-1} is in good agreement with the previously reported spectral range for phenols.[13] No self-association is observed for the 0.01M solution. The broad band near 3480 cm^{-1} in the spectrum of the 0.1M solution suggests the presence of the dimeric 4EP formed through hydrogen bonding.[13 14] Further self-association occurs in the more concentrated solution of 1M as indicated by the very broad IR band near 3335 cm^{-1}.

Figure 3 illustrates the IR spectra of 4EP/DMM mixtures. The broad band near 3393 cm^{-1} can be reasonably attributed to the hydrogen bonded OH absorption since it is not observed in the spectrum of 0.01M 4EP solution and is very weak in the spectrum of 1M DMM solution. The intensity of this H-bonded band increases at the expense of the free OH intensity as the DMM concentration increases.

Similar results are found for 4EP/TEGDME mixtures (Figure 4) for which the hydrogen bonded OH band occurs near 3365 cm^{-1}. However, the intensity of the free OH band decreases at a much faster rate with the ether concentration for TEGDME than for DMM. This is probably due to the fact that there are more basic sites per molecule in TEGDME than in DMM. In addition, Drago[15 16] has demonstrated that the hydrogen bond dissociation energy can be estimated from the frequency shift of the OH stretching from the free OH frequency by the following correlation:

$$-\Delta H \text{ (kcal/mol)} = 0.0103\Delta\upsilon_{OH} \quad (cm^{-1}) + 3.08$$

Table 2 summarizes the frequency shifts and the hydrogen bond dissociation energies for 4EP/DMM and 4EP/TEGDME systems, and for 4EP self-association. The ΔH values calculated from the above equation appear to agree with the literature values for similar systems.[14]

Application of the Binary Interaction Model

The heat-of-mixing of a premixed solution of analogs 1 and 2 with analog 3 simulates the enthalpic effect in mixing a random copolymer with a homopolymer.[17] The heats in such a ternary system can often be estimated from a binary interaction model:

$$B = B_{13}\phi_1 + B_{23}\phi_2 - B_{12}\phi_1\phi_2 \qquad (5)$$

where B is the observed heat effect in mixing the solution, and ϕ_1 and ϕ_2 represent the compositions of the premix.

We can model blends of styrene - vinyl phenol copolymers with PAc using the B_{ij} values listed in Table 2. For VP = 1, S = 2, and Ac = 3, the interaction parameters are B_{12} = 6.9, B_{13} = -7.6, and B_{23} = 1.5. Analysis using equation 5 shows that vinyl phenol levels of 10%v or greater in a copolymer with styrene produce net exothermic mixing (B < 0) in blends with polyacetal. Thus, on this basis, one would

anticipate miscibility between polyacetal and styrene/vinyl phenol copolymers which contain at least 10% vinyl phenol.

The model predicts that miscibility is driven by the combination of a strong favorable interaction between acetal and vinyl phenol units, a relatively weak unfavorable interaction between acetal and styrene units, and a strong unfavorable interaction between vinyl phenol and styrene units.

To test the applicability of equation 5 to hydrogen-bonding systems, we measured the heats-of-mixing dilute solutions of 4EP in EB against DMM. A 4% solution of 4EP in EB mixes exothermically to form DMM-poor mixtures and endothermically to form DMM-rich mixtures as shown in figure 2.[4 5] The binary interaction model slightly overestimates the amount of phenol needed to produce exothermic mixing, consistent with results on similar systems measured in our laboratory. The model, therefore, provides a conservative basis from which to predict the phase behavior of homopolymer and copolymer blends.

Application of the Coleman - Painter approach

Coleman and Painter recently proposed an association model to represent the phase behavior of polymer blends where one polymer self-associates and the second polymer associates with the first.[6 8] Unlike the binary interaction model, this approach does not assume mean field statistics for all interactions and explicitly considers both enthalpic and excess entropic contributions to the excess Gibbs energy. Coleman and Painter have applied this model successfully to blends of PVP and polymers containing ester groups.[18 19] This model should apply as well to blends of PVP with polyethers. However, the requisite equilibrium constant and enthalpy to characterize the hydrogen bonding between polyethers and PVP are unavailable.

Recently Coleman and Painter presented a simplified approach to screen for miscible blends, which embodies the main effects in their rigorous model.[20] The unfavorable dispersive contribution to mixing is estimated from non-hydrogen bonding solubility parameters. This is compared to the expected favorable contribution characteristic for a given class of specific interaction. From group contributions the estimated solubility parameters for PAc and PVP are 10.5 and 11.0 respectively. The estimated solubility parameter for PAc falls within the range of values reported in the literature.[21] Strong hydrogen bonding should readily overcome this relatively small difference in solubility parameters. Therefore, this approach predicts miscibility between PAc and PVP.

CONCLUSIONS

Low molecular weight analogs of polyacetal and poly(vinyl phenol) exhibit large exothermic heats of mixing. FTIR spectroscopy indicates that this specific interaction arises from hydrogen bonding between the ether oxygens and the hydroxyl group of the phenol. These results suggest a strong thermodynamic driving force for polyacetal and poly(vinyl phenol) to form miscible blends.

Low molecular weight analogs of PEO and PVP also show large exothermic heats of mixing. This is consistent with the reported miscibility of PEO/PVP blends. A χ parameter estimated from the analog heats is in excellent agreement with a χ value derived from analysis of melting point depression in the blends.

Application of the binary interaction model of Paul predicts that copolymers of styrene and vinyl phenol containing approximately 10% vinyl phenol units will be thermodynamically miscible with polyacetal. The binary interaction parameters are derived from the heat of mixing measurements. This approach slightly overestimates the amount of phenol needed to produce exothermic mixing of analog solutions.

Analysis using the recently proposed approach of Coleman and Painter also predicts a strong driving force for miscibility between PAc and PVP.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Heats-of-mixing of analogs:

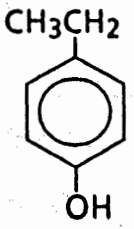
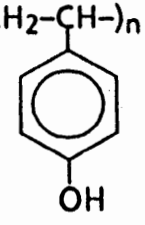
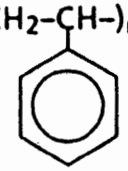
A) DMM vs. EB B) 70%w 4EP in EB vs. EB

C) 64% 4EP in EGDME vs. EGDME

D) 50% 4EP in DMM vs. DMM

Figure 5. Heat-of-mixing of 4% 4EP in EB vs. DMM.

Table 1. Analog and Polymer Structures

Analog	Structure	Polymer	Structure
4-Ethylphenol 4EP		Poly(vinylphenol) PVP	
Dimethoxymethane DMM	$CH_3-O-CH_2-O-CH_3$	Polyacetal PAc	$(-CH_2-O-)_n$
Ethylbenzene EB		Polystyrene PS	
Ethyleneglycoldimethylether EGDME	$CH_3-O-CH_2CH_2-O-CH_3$	Poly(ethyleneoxide PEO	$(-CH_2-CH_2-O-)_n$
Tetraethyleneglycoldimethylether TEGDME	$CH_3-O-(CH_2O-)_4CH_3$	Poly(ethyleneoxide) PEO	$(-CH_2-CH_2-O-)_n$

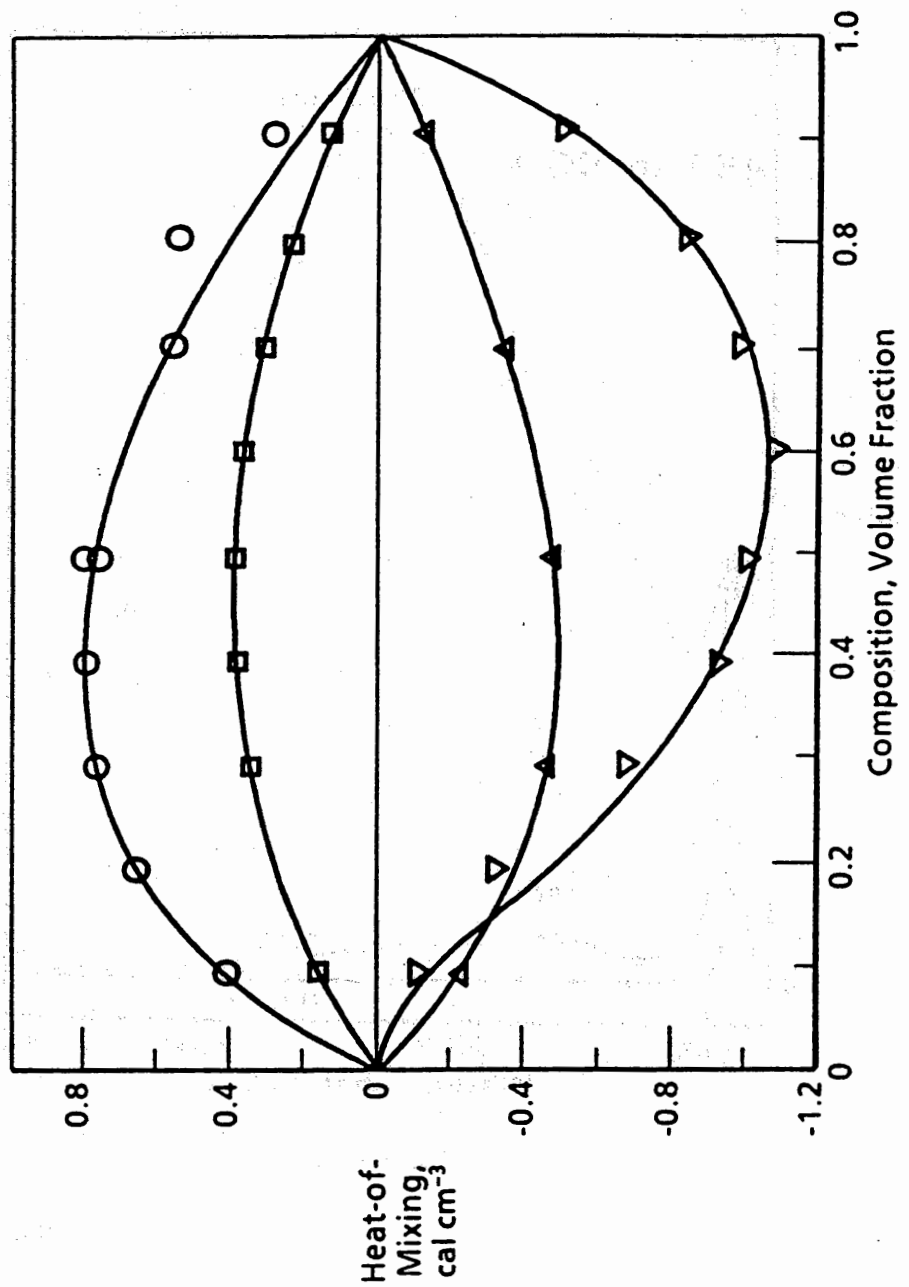
016083-1

Table 2. Interaction Parameters

Analog 1	Analog 2	Polymer Pair	B_{12}, cal cm^{-3}	$\Delta\nu_{OH}$, cm^{-1}	$\Delta H_{H\text{-bond}}$, kcal mol^{-1}
4EP	DMM	PVP-PAc	-7.6	221	5.34
4EP	EB	PVP-PS	6.9		
DMM	EB	PAc-PS	1.5		
4EP	EGDME	PVP-PEO	-10.0		
4EP	TEGDME	PVP-PEO		249	5.64
4EP*	–	PVP-PVP		135	4.47
4EP†	–	PVP-PVP		279	5.93

* *Self-associated through dimers.*
† *Self-associated through multimers.*

016083-2


Heat-of-Mixing, cal cm^{-3}
0.8
0.4
0
-0.4
-0.8
-1.2
0
0.2
0.4
0.6
0.8
1.0
Composition, Volume Fraction
016083-3

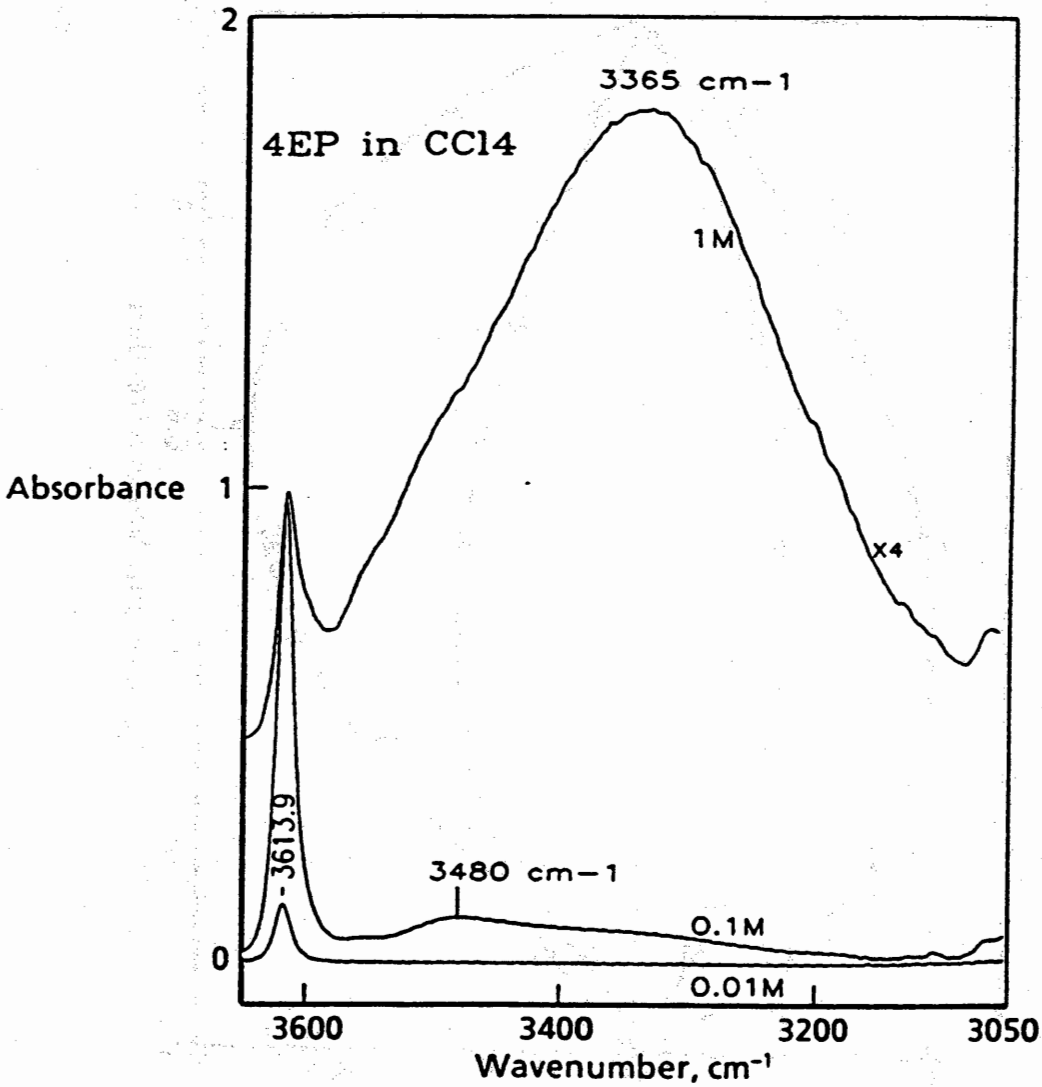


Figure 2.

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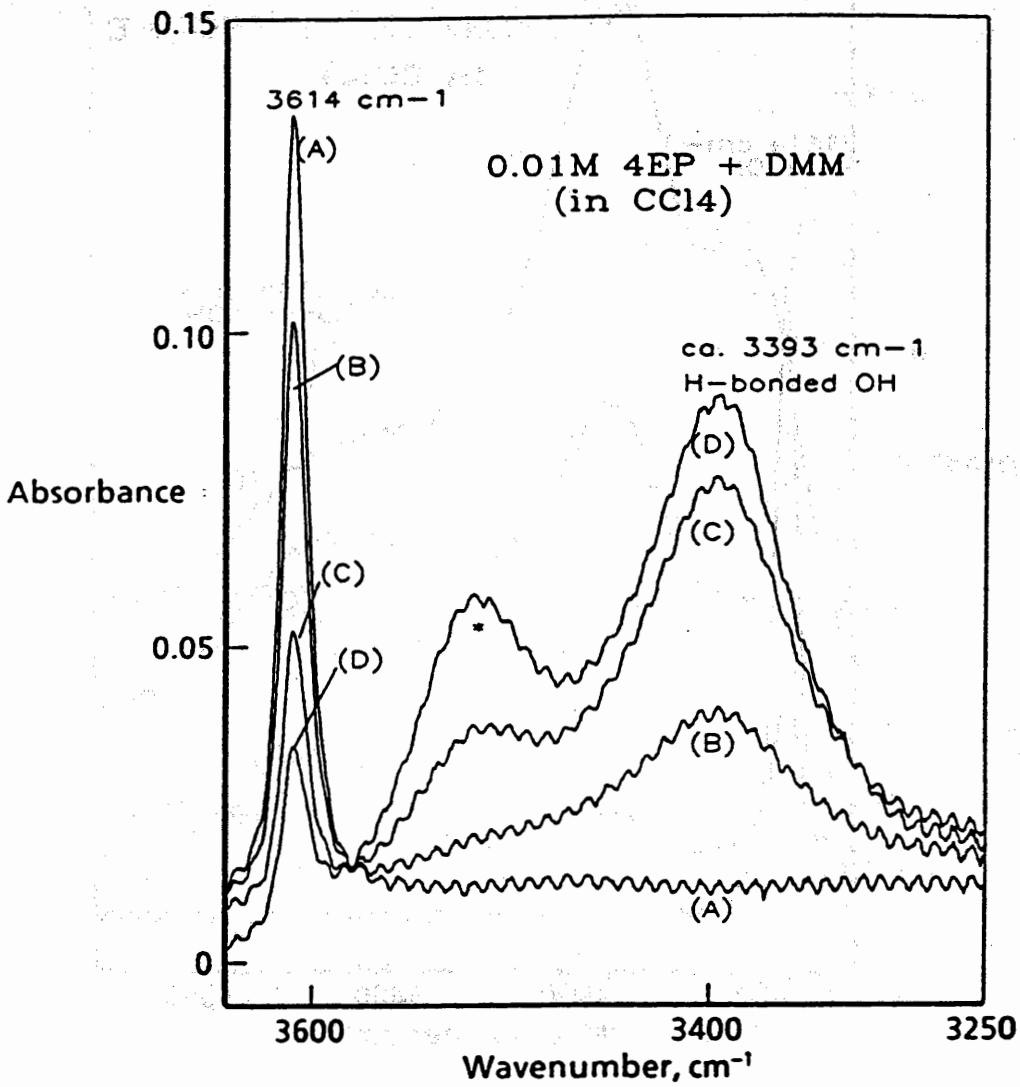

Figure 3.

**IR band due to DMM.*

016083-6

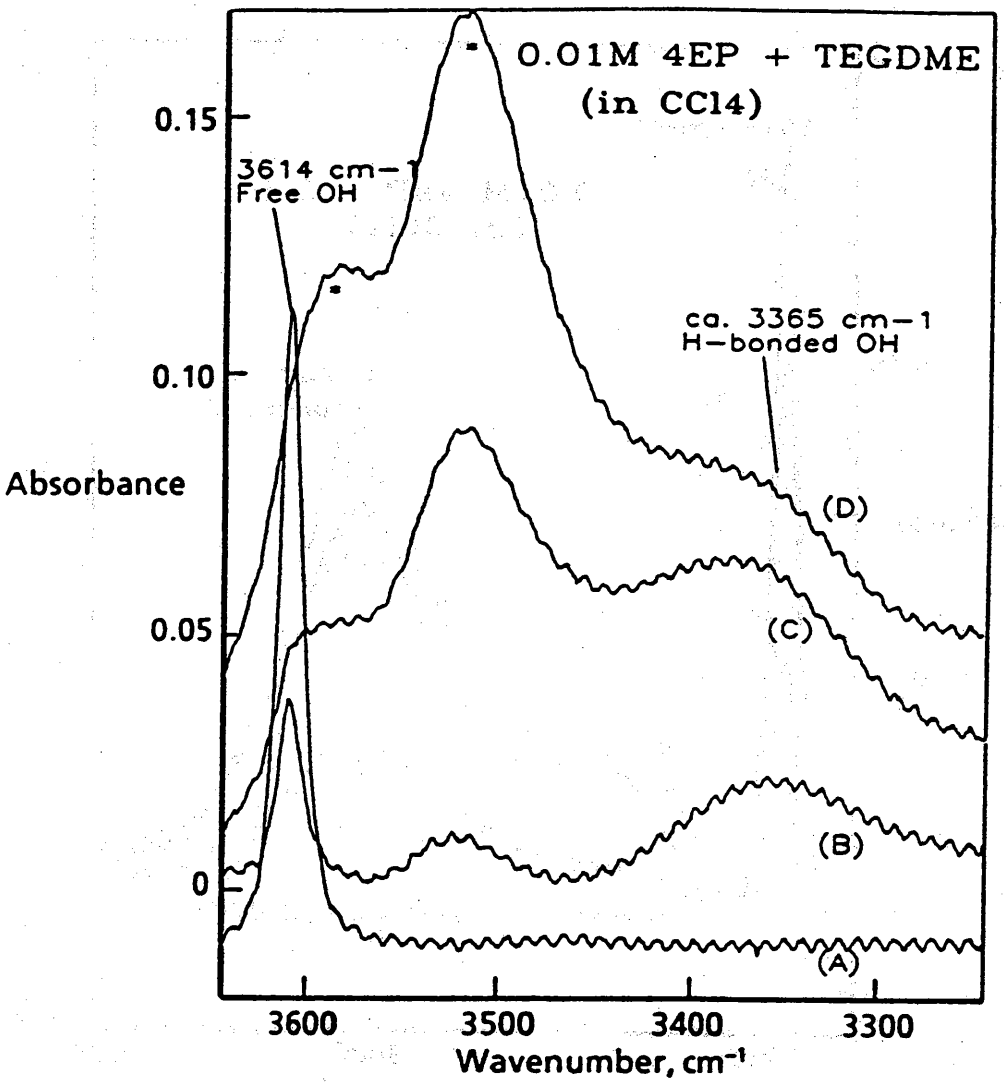

Figure 4.

**IR band due to TEGDME.*

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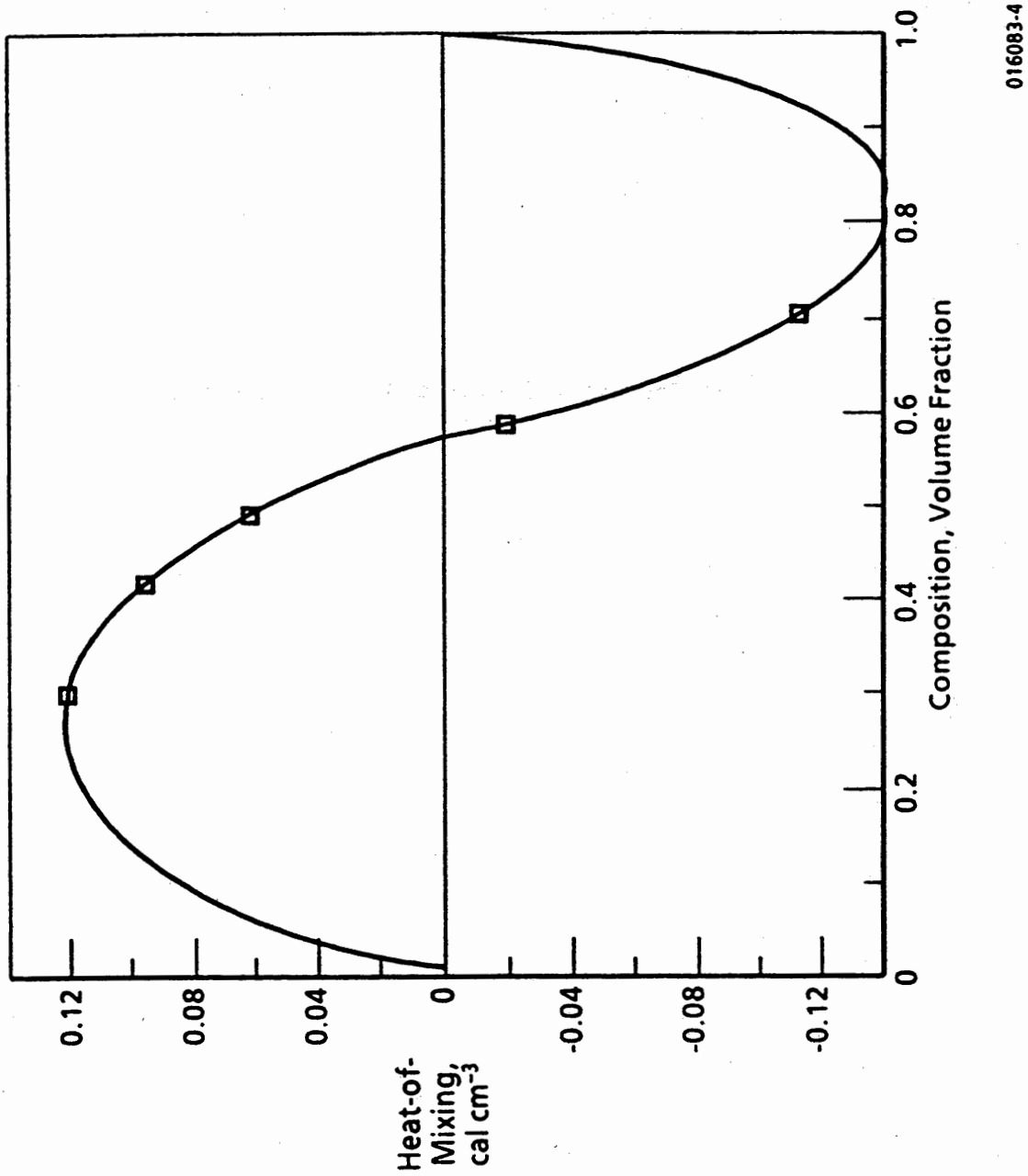
0.12
0.08
0.04
0
-0.04
-0.08
-0.12
Heat-of-Mixing, cal cm^{-3}
0
0.2
0.4
0.6
0.8
1.0
Composition, Volume Fraction
016083-4

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Appendix II

Miscible Polyacetal – Polyvinyl Phenol Blends:
2. Thermo-Mechanical Properties and Morphology

MISCIBLE POLYACETAL/POLYVINYL PHENOL BLENDS: 2. THERMO-MECHANICAL PROPERTIES AND MORPHOLOGY

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ABSTRACT

Blends containing polyacetal copolymer and polyvinyl phenol were prepared by melt compounding and investigated with respect to dynamic mechanical behavior, melting behavior, density, and morphology. Complete miscibility was evidenced by a single, composition-dependant glass transition temperature intermediate between those of the pure components and a substantial depression of the melting point of the crystalline phase. Analysis of the melting point depression yielded an approximate interaction parameter, which was in excellent agreement with that obtained from the calorimetric mixing of chemical analogues. Also in suppport of miscibility was the observation of a significant negative volume-of-mixing. The emergence of a banded spherulitic texture upon blending was also noted. The overall thermal behavior of this miscible system was shown to conform to the theoretical model of Yoon and Kumar.

INTRODUCTION

In the accompanying paper, we demonstrated favorable enthalpies of mixing between acetal and phenol moieties in low molecular weight compounds which act as chemical analogues for the title polymers. These results were discussed in terms of hydrogen-bonding interactions and were used to predict miscibility between polyacetal and polyvinyl phenol.

Polyacetal, or poly(oxymethylene), is a semi-crystalline engineering thermoplastic of considerable commercial importance. Despite this, blends containing this polymer have received very sparse attention in the literature, especially in comparison to other materials within this class [1-5]. Furthermore, no clear case of miscibility in a polyacetal-containing blend has been reported, although limited degrees of compatibility with polyvinyl chloride, polyurethanes, and ionomers have been described [3-5].

The present contribution concerns melt-compounded blends containing a commercial polyacetal and two polyvinyl phenol homopolymers which differ in molecular weight. Miscibility is evidenced by the continuous composition dependance of the major thermal transitions.

EXPERIMENTAL

The materials used in this study are described in Table 1. The polyacetal is an injection molding grade, copolymer-type material, Celcon M-90, obtained from Hoechst-Celanese. NMR reveals that this copolymer contains 2-3% oxyethylene repeat units, the remainder being

oxymethylene. The polyvinyl phenol materials were also obtained from Hoechst-Celanese and were characterized by GPC in N-methyl pyrrolidone.

The blends were prepared by the melt-compounding of pre-dried powder blends using a laboratory scale Baker-Perkins 15 mm co-rotating twin-screw extruder. The screw design, shown in Figure 1, is fully intermeshing and self-wiping and includes a series of mixing paddles, designed for the thorough dispersion of blend components. The extruder was operated at 240°C barrel temperature and 300 RPM screw rotation. The blends were subsequently compression molded at 230°C into plaques which were 0.75 mm in thickness. The molded plaques were subjected to slow cooling between preheated Teflon sheets.

Dynamic mechanical analysis was performed on specimens derived from molded samples. A Polymer Laboratories DMTA operating in the single cantilever beam mode at a frequency of 10 Hz and a heating rate of 3°C/min was used. Calorimetric analysis was also performed on molded samples using a Perkin-Elmer DSC-7 scanning at 20°C/min between -40°C and +220°C. Optical microscopy was performed on thin specimens microtomed from the molded plaques. Specific volume measurements were performed at 25°C in a density gradient column using sodium bromide solution in distilled water.

RESULTS AND DISCUSSION

Dynamic Mechanical Behavior

The dynamic mechanical spectrum of unblended polyacetal prepared according to our protocol is shown in Figure 2. Three thermal transitions below the melting point are in evidence. The transition at

125°C, α, has been clearly associated with molecular motion within the crystalline phase [6]. The question of whether the transition at -60°C, γ, or the one at -6°C, β, corresponds to the glass transition of the amorphous phase has been a matter of some controversy [6,7]. The transition at -60°C is the dominant one in the dynamic mechanical spectrum. However, the value of -6°C is consistent with the extrapolation of T_g's within the homologous series of poly(alkylene ethers) and with the overall dynamic mechanical behavior of a series of polyacetal copolymers which vary in oxyethylene content [8]. The assignment of the glass transition temperature associated with the amorphous phase of polymers which possess a high degree of crystallinity is very often an ambiguous and controversial matter. At present, we prefer to associate the β transition which we observe at -6°C with the glass transition of polyacetal.

The dynamic mechanical spectra of the unblended polyvinyl phenol homopolymers could not be obtained because these materials were excessively brittle. Nevertheless, the glass transition temperatures of these wholly amorphous materials could be unequivocally identified by differential scanning calorimetry and are given in Table 1. We expect that the equivalent T_g values, if measured by dynamic mechanical means, would be somewhat higher because of visco-elastic frequency-temperature shifts.

Dynamic mechanical analysis of melt-compounded polyacetal/polyvinyl phenol (PAc/PVP-7k) blends provided compelling evidence for miscibility within the amorphous phase. In Figure 3, the dynamic mechanical loss tangent is plotted against temperature for blends of each composition. The dominant feature of the mechanical spectra is a relaxation peak, the magnitude and temperature of which increases steadily as the PVP content of

the blend increases. The identification of this thermal transition with the glass transition of the blend follows from the observation that the transition temperature steadily approaches the T_g of pure PVP as the blend becomes rich in PVP. Figure 4 demonstrates the nearly linear T_g-composition relationship which is both characteristic and diagnostic of a blend system which is miscible [9].

Figure 5 shows loss tangent curves for two blends which contain high molecular weight polyvinyl phenol (PVP-50k). In these cases the loss tangent exhibits a very broad plateau. Nevertheless, the approximate mid-point of the plateaus appear to follow the expected composition-T_g relationship as given in Figure 4, suggesting that perhaps equilibrium miscibility is being approached. The melt processing of these higher molecular weight polyvinyl phenol blends was made difficult by high melt viscosities and the rather narrow melt temperature window which these blends will tolerate. The dynamic mechanical results for all of the blends which were studied are summarized in Table 2.

Melting and Crystallization Behavior

The present blend system falls within the class of miscible semi-crystalline/amorphous blends. In such systems (e.g. PEO/PMMA, PCL/PVC, PVF_2/PMMA) it is typical for the crystallizable component, if present in an appreciable concentration, to be partitioned between a pure crystalline and a mixed amorphous phase [10-12] (and perhaps a third phase, discussed later). The crystalline phase is affected by changes in the mixed amorphous phase with which it is in (pseudo)equilibrium. This effect is manifested by reductions of the

melting point and of the degree of crystallinity. In the present case both phenomena were observed.

DSC thermograms, showing crystalline melting endotherms, are given for blends of various composition in Figure 6. The results are summarized in Table 3. The enthalpies of melting upon heating and of crystallization upon cooling at constant rate both decrease as PVP is added to the blend. Figure 7 shows the degree of crystallinity, which has been calculated from the melting enthalpies and normalized for the polyacetal content of the blend, plotted against composition. The degree of crystallinity remains virtually constant up to a PVP content of about 40 wt%. Upon further addition of PVP, the crystallinity of the PAc component is greatly reduced. Figure 8 gives the peak temperatures of melting and of crystallization as a function of blend composition. Both are significantly reduced as the PVP content increases. Thus crystallization is impeded in the presence of the amorphous component, which implies miscibility in the melt.

It is known that the interaction strength in a polymer blend can be quantified by an analysis of the equilibrium melting point depression in the case where one of the components is crystallizable [13]. A Hoffman-Weeks extrapolation of melting data is most frequently used to obtain equilibrium melting temperatures. In the present case, however, the data from Table 3 were used without extrapolation and were analyzed using the expression of Nishi and Wang [14], given by:

$$(1/T_m) - (1/T_m)_o = [(R)(V_c)/(H_f)(V_a)][\chi_{12}][\Phi_2]^2 \qquad (1)$$

The parameters are explained in Table 4. In Figure 9, the left side of the equation is plotted against the square of the volume fraction of the polymeric diluent, which is PVP in this case. The volume of PVP within the amorphous phase was calculated from the blend weight fraction, the degree of crystallinity from DSC, and the component densities in Table 1. Although the melting data used are not equilibrium values, the resultant plot, shown in Figure 9, exhibits remarkable linearity over a broad range of composition. Thus we suggest that this slope reflects a useful estimate of the strength of the physical interaction within the amorphous phase of the blend. The calculated Van Laar interaction parameter, B_{12}, is -10.7 cal/cm^3, which corresponds to a Flory-Huggins interaction parameter, χ_{12}, of -1.25 at the melting temperature, if we take the reference volume to be the molar volume of one PVP repeat unit (see Table 4). These values are in excellent agreement with those determined by the calorimetry of mixtures of low molecular weight chemical analogues, as discussed in the accompanying paper. Thus, we confirm in the polymer mixtures, as in the analogue mixtures, that the blend interaction is relatively strong and consistent with the hypothesis of hydrogen bonding.

Blend Morphology

The morphology of the blends was investigated by optical microscopy of sections microtomed from the central region of compression molded specimens. Figure 10A shows a micrograph of unblended polyacetal, which reveals a rather disordered spherulitic structure typical for a non-isothermally melt-crystallized polymer. In Figure 10B, an 80/20

PAc/PVP-7k blend also exhibited this morphology. However, as Figure 10C demonstrates, a 50/50 PAc/PVP-7k blend exhibited larger spherulites and a very marked ringed texture within the spherulitic super-structure. Such a "ringed" or "banded" texture arises from a regular and periodic twisting of crystalline lamellae as they grow in the radial direction [15].

Previous studies of other semi-crystalline/amorphous polymer blends which are known to be miscible (e.g. PCL/PVC and PVF_2/polybutyrolactone) have also shown the emergence of banded textures within spherulites formed from the blends. These textures were not apparent in spherulites formed from the pure semi-crystalline component [16-18]. In these cases the ring spacing (periodicity) of the bands tends to be a function of blend composition. Thus, the morphology seen in Figure 10C may be an indicator of miscibility in the melt state. Furthermore, the spherulites observed in the blends are fully impinged and volume-filling indicating that the amorphous component becomes fully incorporated within the spherulitic super-structure. A detailed SAXS analysis is needed to determine specifically how the amorphous component is arranged with respect to the crystalline lamellae.

In a 30/70 PAc/PVP-7k blend, no evidence of spherulitic structures or of optical birefringence could be detected. We attribute this to the low level of crystallinity in this blend.

Specific Volume

Polymer blends which are miscible as the result of strong specific interactions often exhibit negative volumes-of-mixing [19,20]. That is, strong interactions promote shorter intermolecular distances at the expense of free volume. Thus, significant negative deviation from additivity of specific volume in a polymer blend system provides an indication of such interactions. In the present case of PAc/PVP blends, we expect that strong intermolecular hydrogen bonding will give rise to a negative specific volume-of-mixing.

We define the specific volume-of-mixing, ΔV_m, as:

$$\Delta V_m = V_{blend} - V_{ideal} \qquad (2)$$

where V_{blend} is the experimental specific volume of the blend and V_{ideal} is the specific volume expected from perfect additivity of the pure components, which is given by:

$$V_{ideal} = (w_1)(V_1) + (w_2)(V_2) \qquad (3)$$

where w_i and V_i correspond to weight fractions and specific volumes, respectively of pure blend components 1 and 2. In the present case, the semi-crystalline nature of polyacetal complicates our analysis because the specific volume of the polyacetal component depends strongly upon its degree of crystallinity, which varies with the composition of the blend. However, we can correct for this effect by considering the measured degree of crystallinity (from Figure 7) and

assuming that the corrected specific volume of the polyacetal component in the blend is additive:

$$V_{PAc} = (w_c)(V_c) + (w_a)(V_a) \qquad (4)$$

where the subscripts c and a correspond to the pure crystalline and amorphous phases of polyacetal. V_c can be calculated from the crystalline unit cell and is reported to be 0.671 cm^3/g [21,22]. For internal consistency we calculated V_a by solving equation 4 for V_a with our measured data for the pure polyacetal control. The resultant V_a, 0.760 cm^3/g, is in excellent agreement with published literature values [21].

In Figure 11, the corrected specific volume-of-mixing normalized with respect to the ideal specific volume, $\Delta Vm/V_{ideal}$, is plotted as a function of blend composition for PAc/PVP-7k blends. All the blend compositions exhibited a specific volume-of-mixing which was reasonably large and negative in sign. The volume-of-mixing appeared to reach a maximum absolute valve in the PVP-rich composition region. These results are consistent with strong hydrogen bonding interactions and the resultant large, negative value of χ_{12} for the blend.

Phase Compositions

Returning briefly to the relationship between the glass transition temperature and the blend composition, given in Figure 4, it may be pointed out that the T_g's of the blends do not approach that of pure polyacetal as the PVP content of the blend approaches zero. Such an observation was made previously in the case of PVF_2/PMMA blends

[23,24], an analogous system known to be both crystallizable and miscible in the amorphous phase. In order to rationalize this T_g-composition relationship, one may invoke the model of Yoon and Kumar who propose three phases for semi-crystalline polymers in general and for blends of this type in particular [25,26]. In addition to pure crystalline and mixed, truly amorphous phases, Yoon proposes an interphase. This interphase is a disordered phase immediately adjacent to the crystal in which molecular motion is strongly suppressed as a result of the flux of chains which are anchored firmly to the crystal surface. The presence of this disordered yet immobile fraction is useful to explain many of the characteristics of semi-crystalline polymers and their miscible blends.

An important characteristic of this interphase, in the case of polymer blends, is that it is unable to accomodate any added amorphous component, even when the component is miscible in the mobile amorphous phase. As a result, the mixed amorphous phase becomes richer in the added miscible component than would be expected from a simple correction based upon the degree of crystallinity.

The present data for PAc/PVP blends can be described within the framework of this theory if one assumes that the composition of the truly amorphous phase can be approximated by fitting the measured glass transition temperature to the Fox equation given by:

$$1/T_{g(blend)} = w_1/T_{g1} + w_2/T_{g2} \qquad (5)$$

where w_i's are weight fractions and the subscripts denote the blend components. We have used pure component T_g values of -6°C and +165°C

for polyacetal and polyvinyl phenol, respectively. Then by subtracting the fraction of the crystalline phase derived from DSC measurements, one is left with an interphase fraction.

Figure 12 shows the calculated weight fraction of each phase as a function of blend composition. The fraction of crystalline material drops off sharply and the fraction of mixed amorphous material rises steeply as the PVP content increases. However, the calculated fraction of interfacial material (approximately 20%) remains relatively insensitive to blend composition. This result is similar to that found for PEO/PMMA and other blend systems and is also expected from theoretical considerations [27,28].

CONCLUSIONS

Miscibility of the polyacetal/polyvinyl phenol blend system is evidenced by a single glass transition temperature, measured by dynamic mechanical means, which is smoothly and strongly dependant upon blend composition. The specific nature of the observed composition dependance of the glass transition temperature was interpreted within the framework proposed by Yoon and Kumar.

A significant melting point depression of the polyacetal crystalline phase was observed, the magnitude of which suggests strong physical interaction in the blend. Further analysis yielded an approximate B_{12} value of -10.7 cal/cm^3 and χ_{12} interaction parameter of -1.25, which is in good agreement with analogue calorimetry experiments performed on model compounds.

A substantial negative volume-of-mixing was measured for blends across the full composition range, suggesting strong physical interactions.

Spherulites found in blends in the intermediate composition range were volume-filling and larger than those found in pure polyacetal which was subject to the same thermal history. Furthermore, a well-developed "banded" texture was observed in blend spherulites which was not found in those of pure polyacetal.

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Table 1. Materials used in this study.

Designation	Description	M_n*	M_w*	T_g	T_m	density
PAc	Polyacetal copolymer	-	-	(-6°C)	170°C	1.402 g/cm^3
PVP-7k	Polyvinyl phenol	8700	17,700	153°C	-	1.163 g/cm^3
PVP-50k	Polyvinyl phenol	50,500	115,000	179°C	-	1.189 g/cm^3

* GPC in N-methyl pyrrolidone expressed relative to polystyrene standards

Table 2. Dynamic mechanical transition temperatures of PVP/PAc blends.

Composition (PVP/PAc wt/wt)	PVP MW	α	β	γ
0/100	-	125°C	-6°C	-60°C
10/90	7k	120°C	83°C	-57°C
20/80	7k	-	92°C	-57°C
30/70	7k	-	103°C	-56°C
40/60	7k	-	113°C	-55°C
50/50	7k	-	132°C	-53°C
70/30	7k	-	141°C	-52°C
100/0	7k		too brittle	
20/80	50k	-	100°C*	-58°C
40/60	50k	-	120°C	-51°C
100/0	50k	-	too brittle	-52°C

* transition was very broad (plateau 70°C to 130°C).

Table 3. Differential scanning calorimetry results for PVP/PAc blends.

Composition	PVP-MW	Heating		Cooling	
		T_m	ΔH_m	Tc	ΔH_c
(PVP/PAc wt/wt)		(°C)	(J/g)	(°C)	(J/g)
0/100	-	169.6	171.8	141.3	144.7
20/80	7k	168.0	138.6	141.5	130.2
40/60	7k	162.4	100.3	133.4	91.4
50/50	7k	158.8	71.2	81.4	26.2
30/70	7k	142.9	11.5	-	0.0
20/80	50k	167.2	137.5	138.7	120.8
40/60	50k	166.5	84.6	134.6	70.1

Table 4. Molecular parameters used for analysis of PAc/PVP blends.

Parameter	Quantity	Value
H_f	Heat of Fusion of pure PAc crystals	9.79 kJ/mol* (326 J/g)
V_c	Molar volume of PAc repeat unit in crystalline phase	20.1 cm^3/mol*
V_a	Molar Volume of PVP repeat unit in amorphous phase	103 cm^3/mol*
B_{12}	Van Laar Interaction Parameter	-10.7 cal/cm^3
X_{12}	Flory-Huggins Interaction Parameter (refered to PVP molar volume)	-1.25

* from or derived from data in References 21 and 22

Table 5. Specific volumes of PAc/PVP blends.

Composition (PVP/PAc wt/wt)	PVP-MW	PAc Crystallinity (%)	V_{blend} (cm^3/g)	V_{ideal} (cm^3/g)	ΔV_m (cm^3/g)
0/100	-	53	0.713	0.713	0
10/90	7k	-	0.724	0.728	-0.004
20/80	7k	53	0.736	0.742	-0.006
30/70	7k	-	0.745	0.757	-0.012
40/60	7k	51	0.762	0.772	-0.010
50/50	7k	44	0.774	0.790	-0.016
70/30	7k	12	0.806	0.827	-0.021
100/0	7k	-	0.860	0.860	0
20/80	50k	53	0.738	0.739	-0.001
40/60	50k	43	0.767	0.770	-0.003
100/0	50k	-	0.841	0.841	0

FIGURE CAPTIONS

Figure 1. Diagram of the extruder screw design used for melt compounding throughout this study.

Figure 2. Dynamic mechanical spectrum of the unblended polyacetal constitiuent. The three thermal transitions are labelled α, β, and γ.

Figure 3. Dynamic mechanical loss tangent, tan delta, as a function of temperature for a series of PAc/PVP-7k blends.

Figure 4. Glass transition temperature as a function of blend composition. Blend T_g's were determined from dynamic mechanical measurements, whereas the T_g of neat PVP was determined from DSC.

Figure 5. Dynamic mechaical loss tangent, tan delta, as a function of temperature for two PAc/PVP blends containing high molecular weight PVP (PVP-50k).

Figure 6. DSC thermograms, upon heating at 20°C/min, for a series of PAc/PVP-7k blends, showing melting endotherm of PAc crystalline phase.

Figure 7. The degree of crystallinity of the polyacetal component as a function of blend composition. The values were calculated from DSC melting endotherms and normalized for polyacetal content.

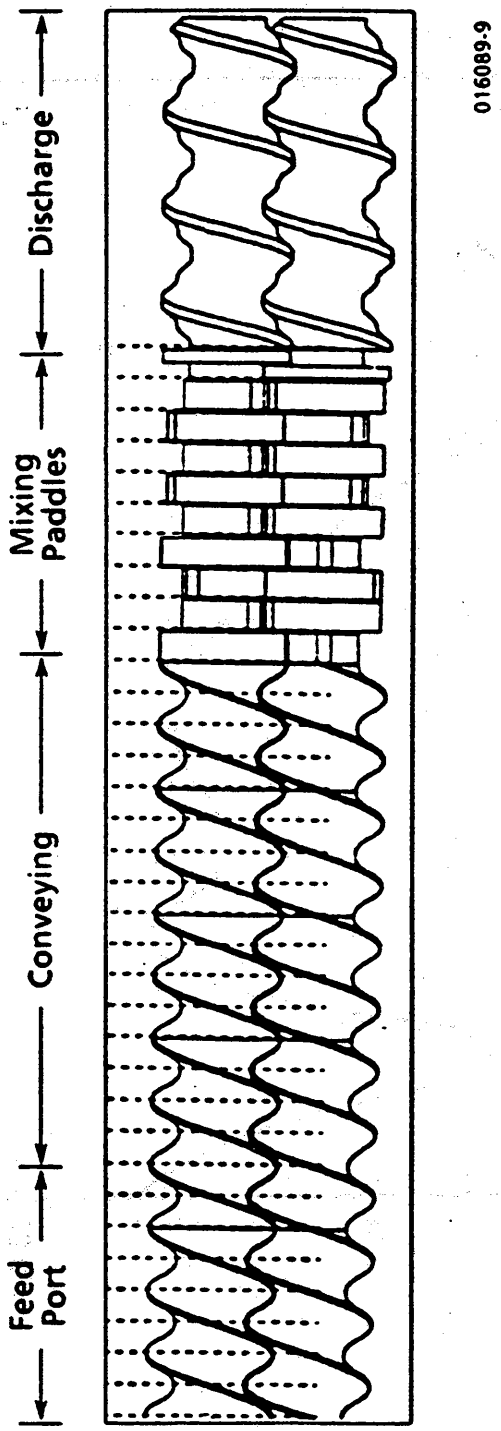
Figure 8. Temperature of melting (upon heating) and of crystallization (upon cooling) from DSC as a function of blend composition.

Figure 9. Melting point depression versus the square of the volume fraction of the non-crystallizable component (PVP-7k).

Figure 10. Optical micrographs of microtomed sections obtained from compression molded samples and viewed between crossed polars: A) 100/0 PAc/PVP-7k, B) 80/20 PAc/PVP-7k, C) 50/50 PAc/PVP-7k.

Figure 11. Specific volume-of-mixing normalized with respect to the ideal specific volume, $\Delta V_m/V_{ideal}$, as a function of blend composition.

Figure 12. Calculated weight fractions of crystalline PAc phase (W_c), truly amorphous phase (W_a), and interphase (W_i) as a function of the total blend composition.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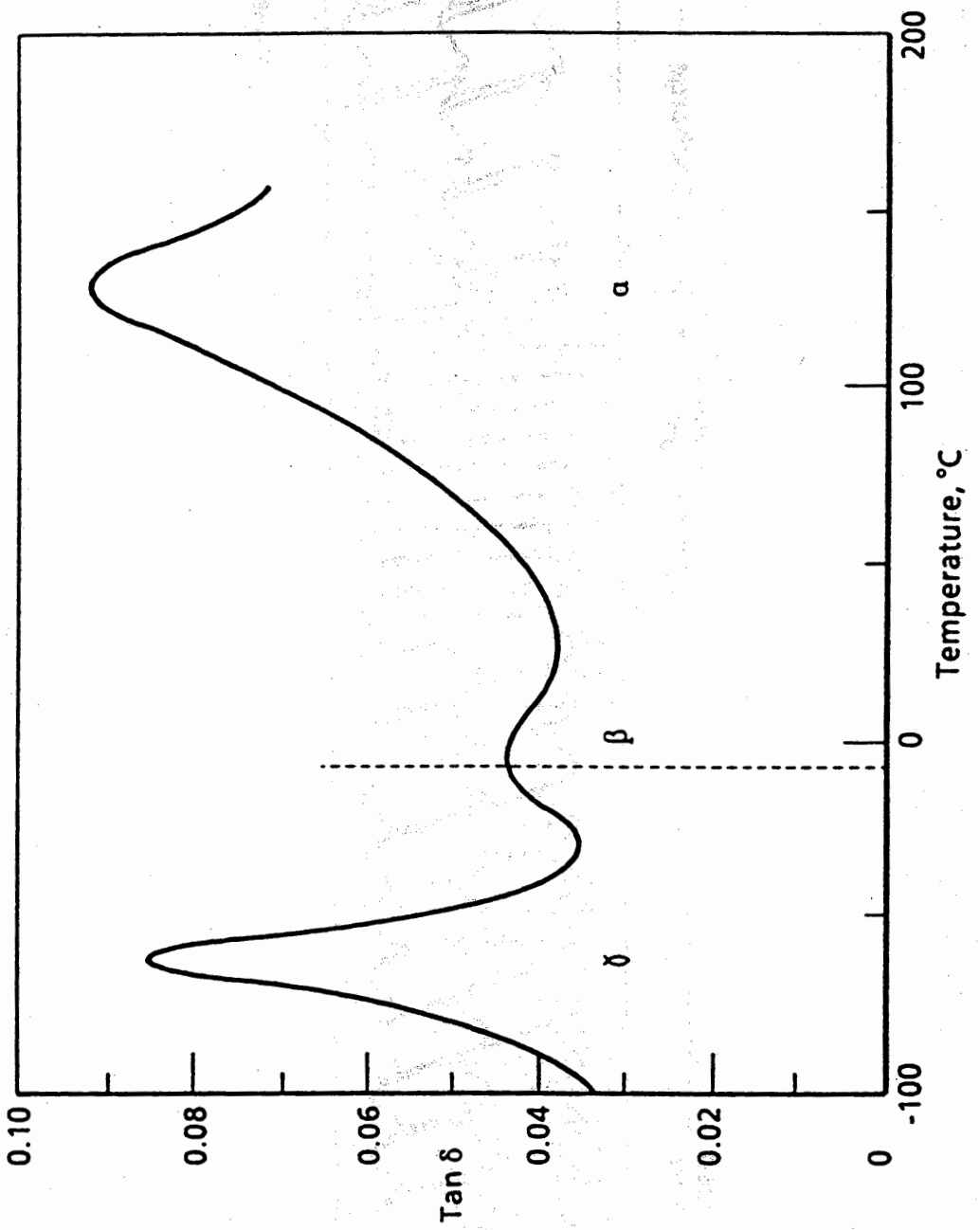
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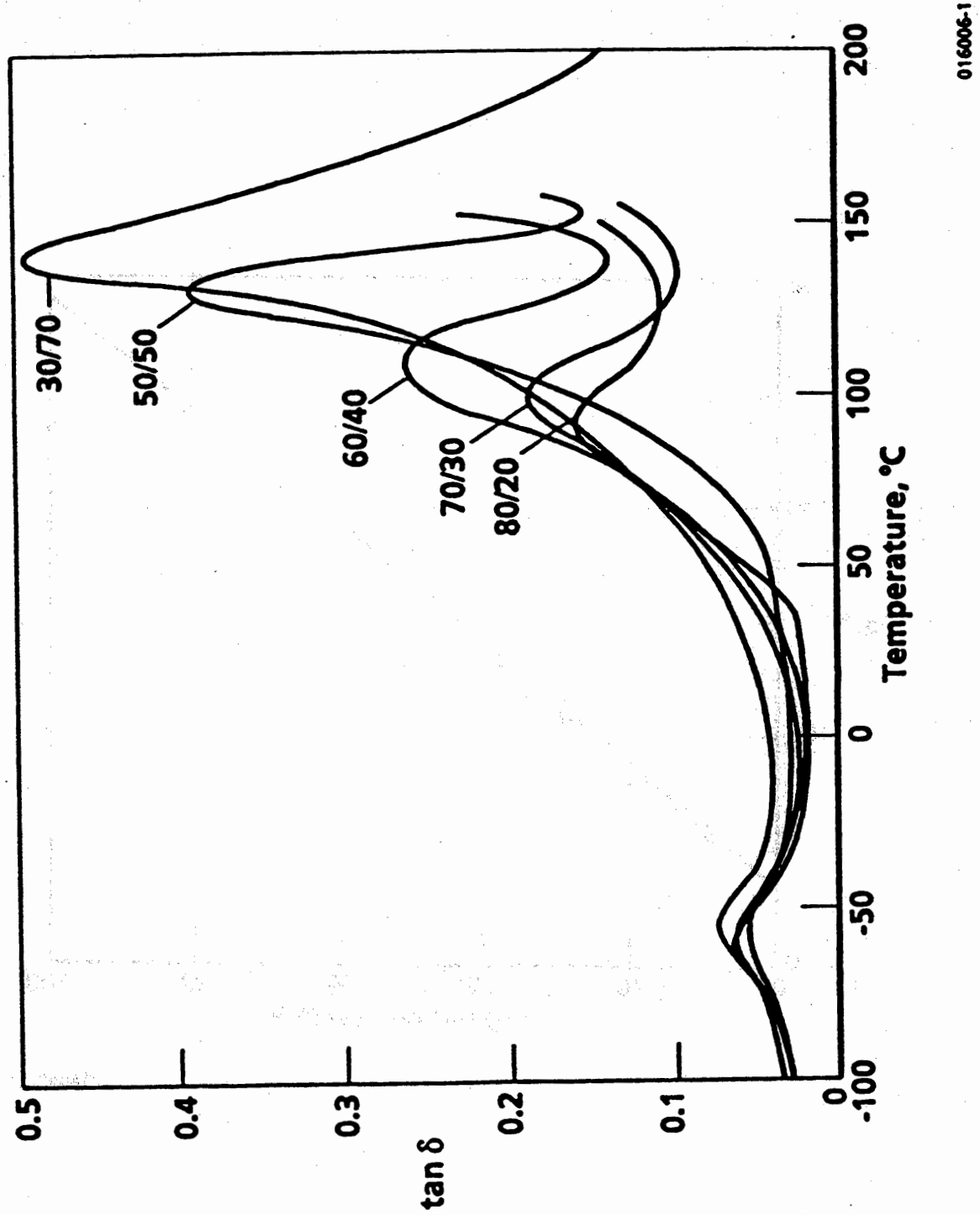
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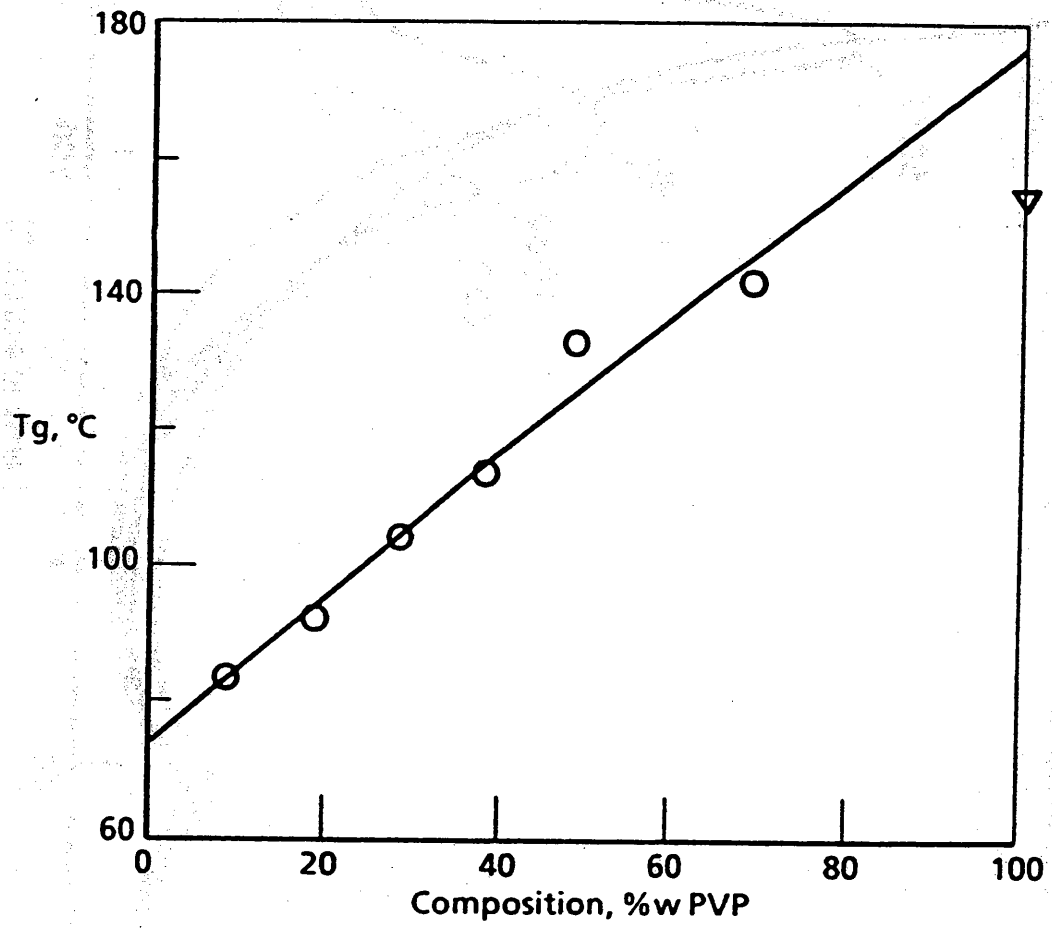
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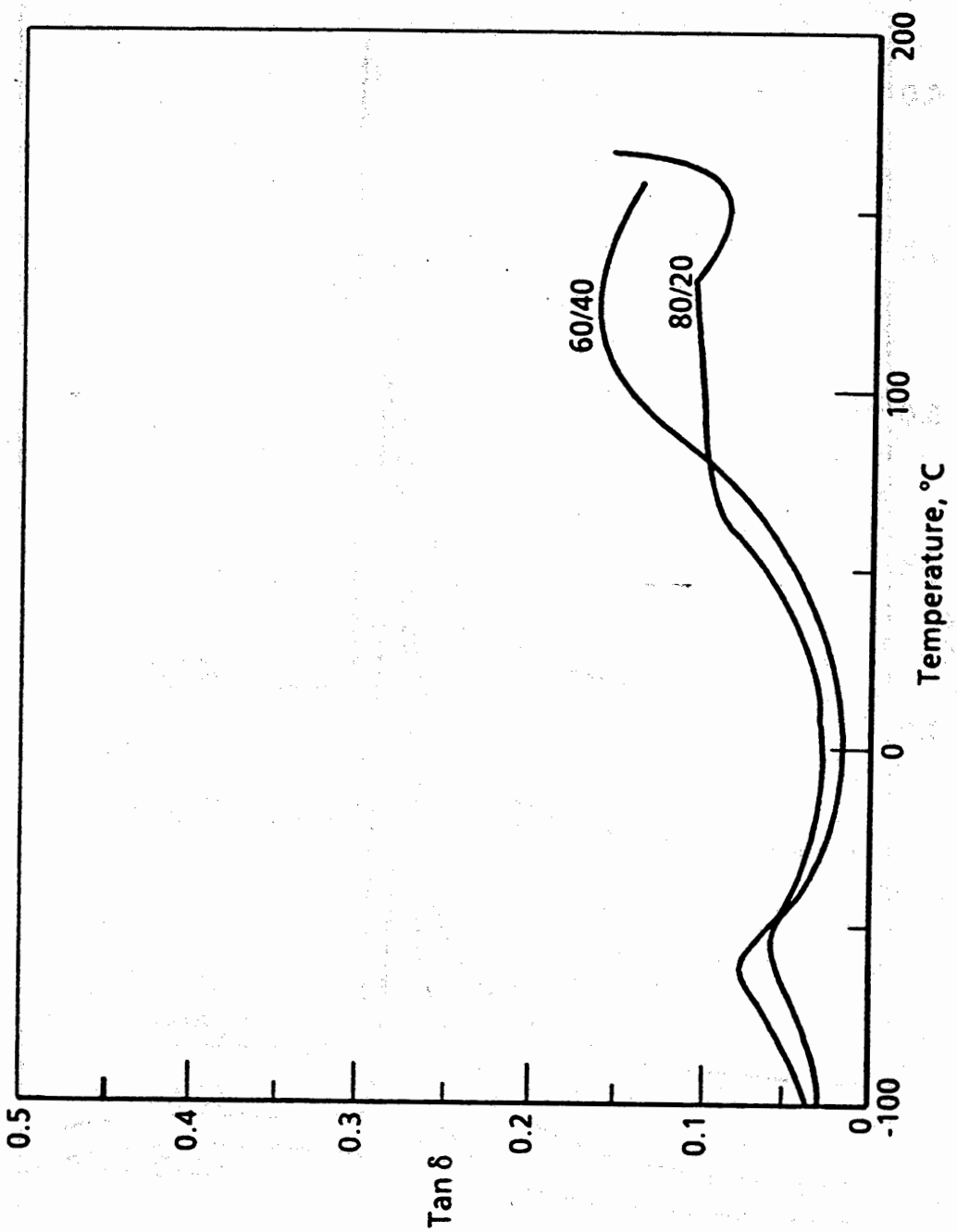
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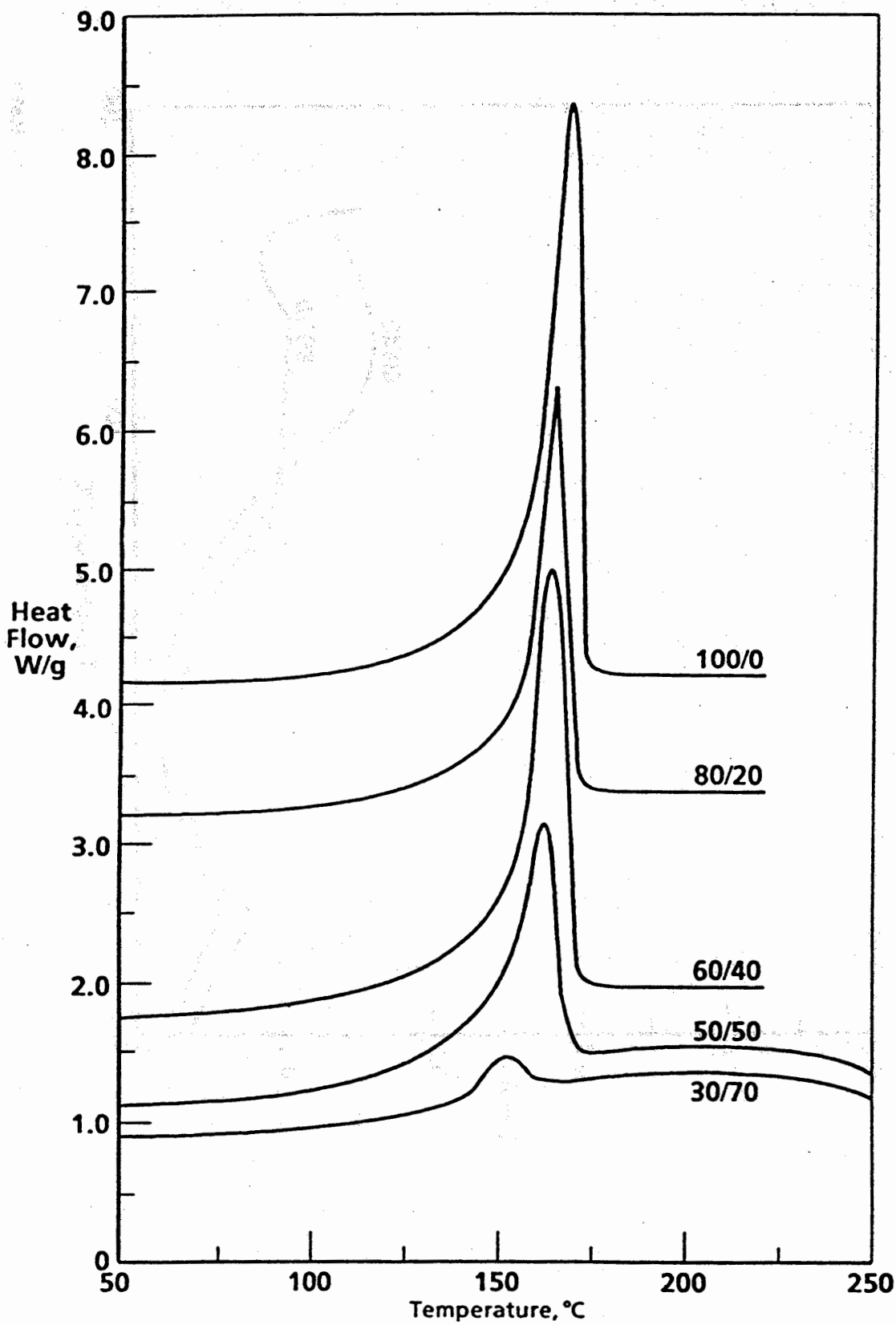
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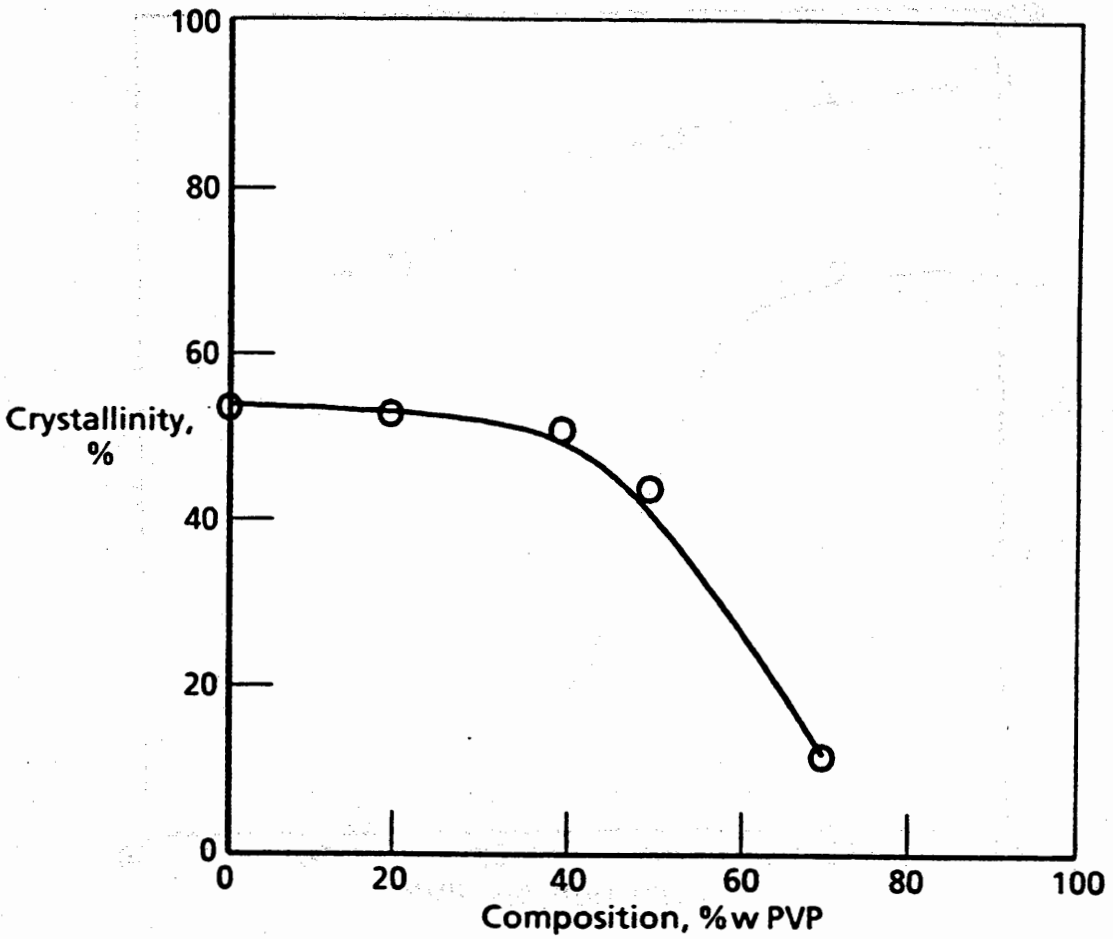
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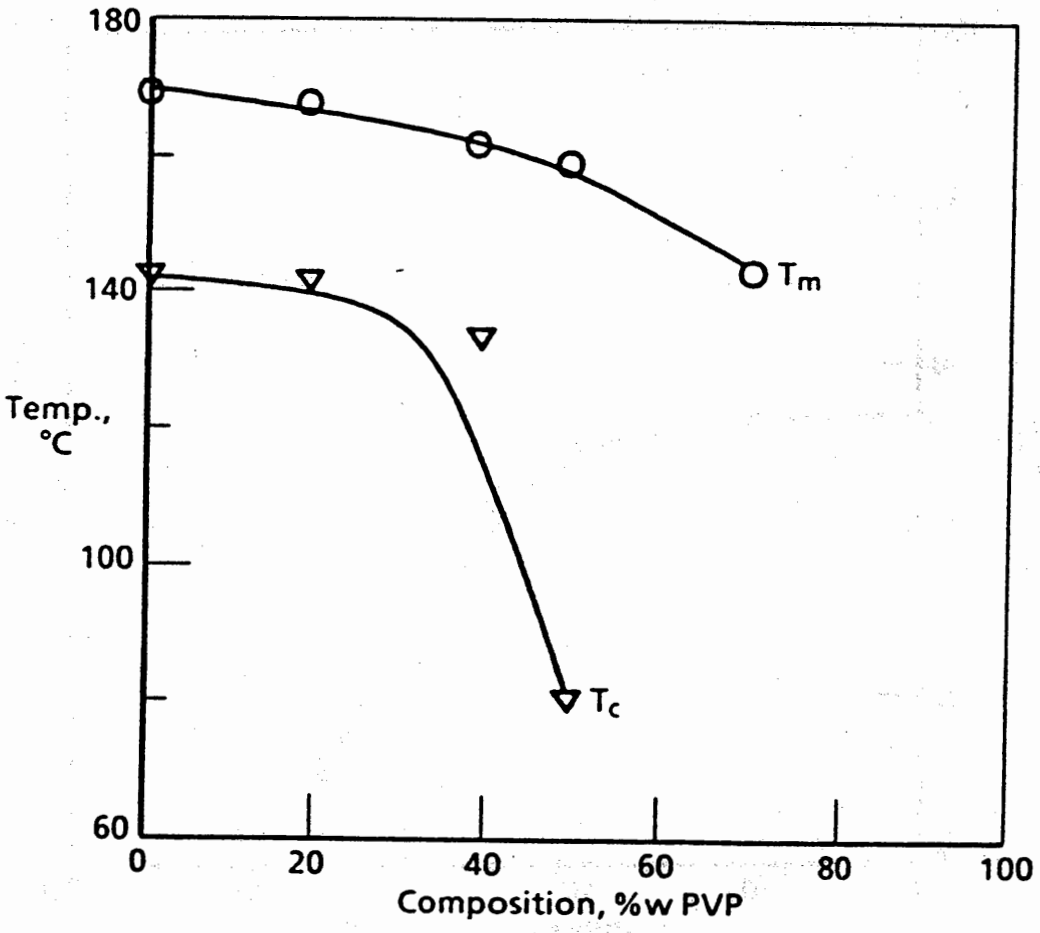
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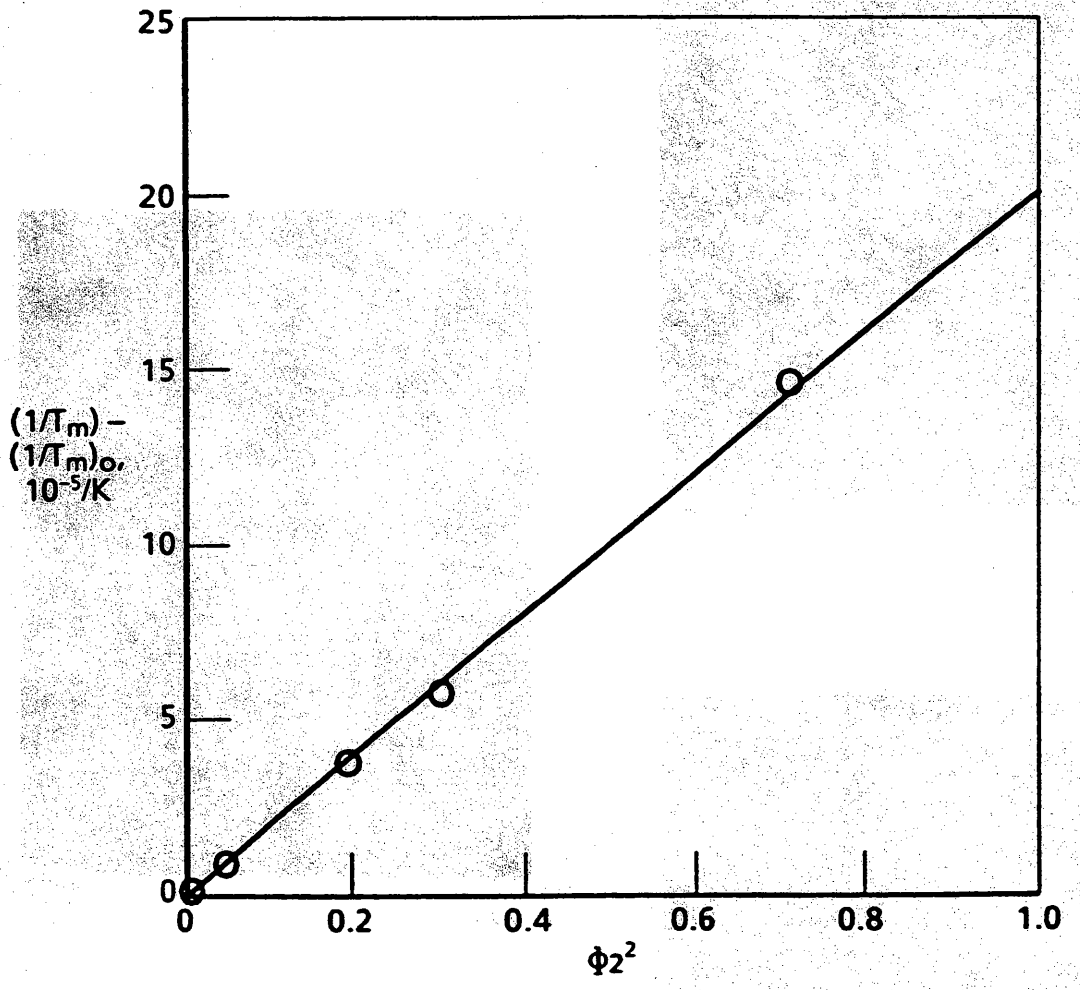
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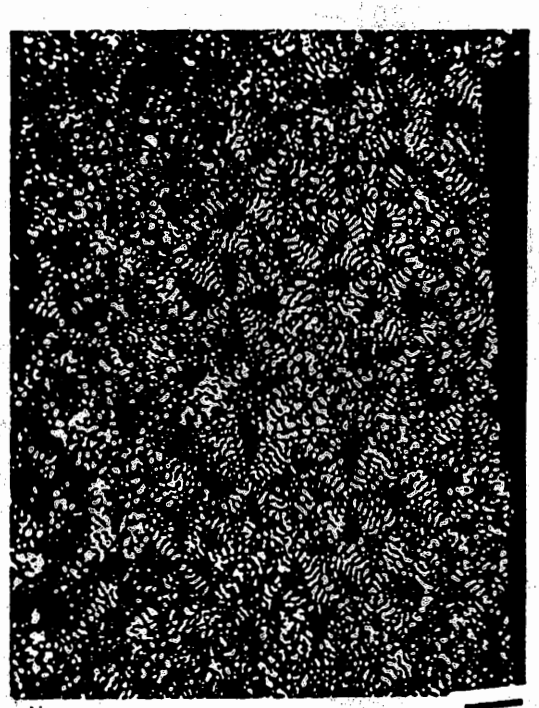
016089-6

← 10B



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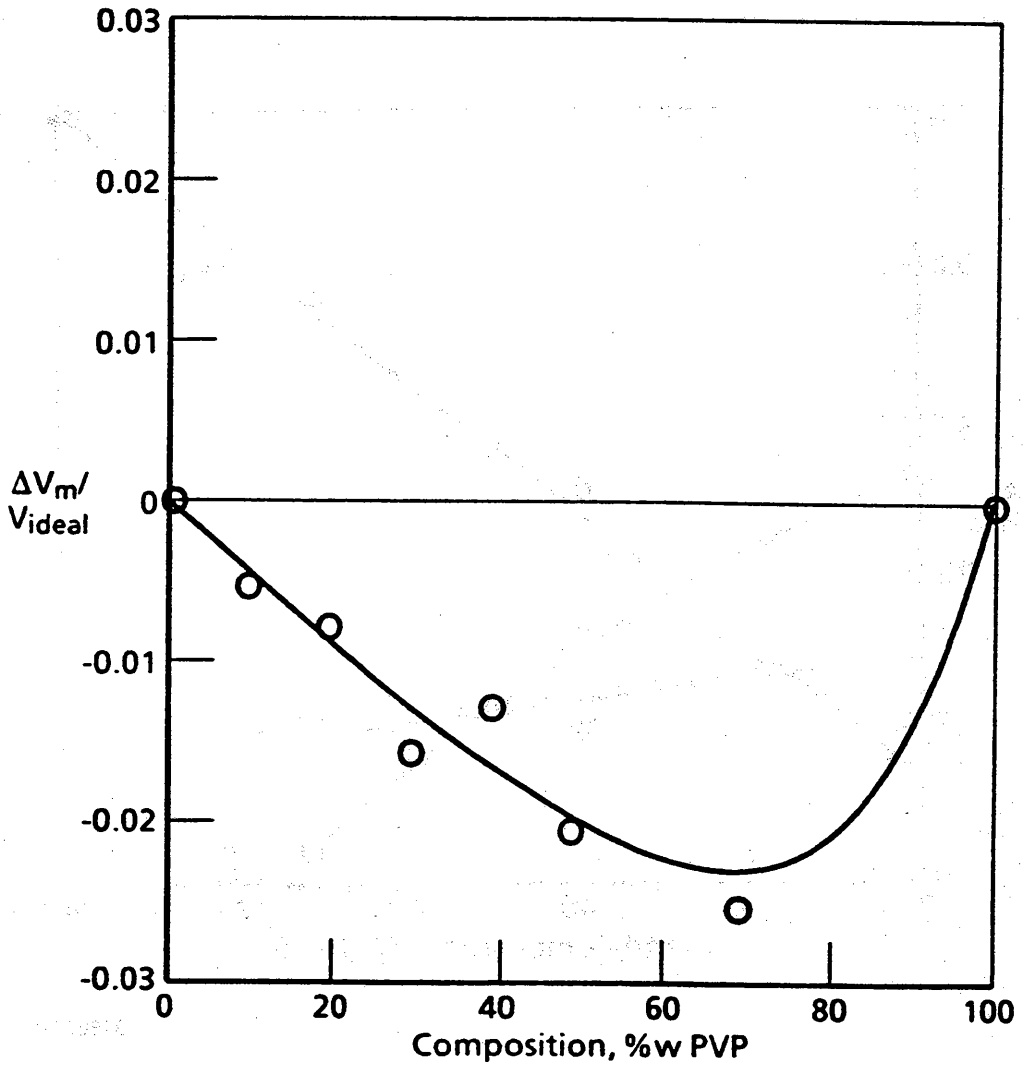
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ΔVm/
Videal
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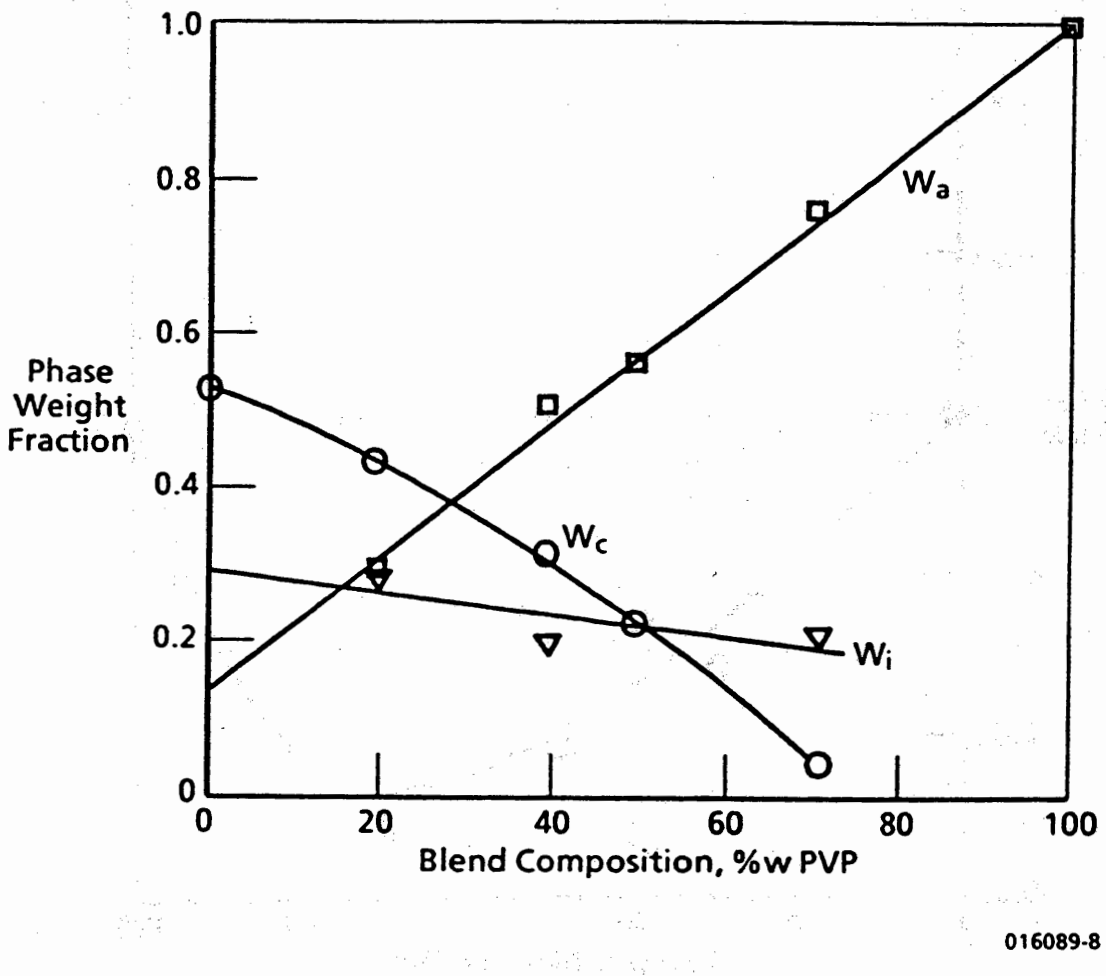
20
40
60
80
100
Composition, %w PVP
016089-7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100
Blend Composition, %w PVP
016089-8

Appendix III

Miscible Blends Between Polyacetal and a Styrene/Vinyl Phenol Copolymer

WRC 2436

MISCIBLE BLENDS BETWEEN POLYACETAL AND A STYRENE/VINYL PHENOL COPOLYMER

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ABSTRACT

Blends containing polyacetal and a random sytrene-vinyl phenol copolymer consisting of 35 mol% vinyl phenol segments were prepared by melt mixing and found to exhibit miscibility within the amorphous phase. The blends exhibited a single, composition-dependent glass transition temperature as determined by dynamic mechanical measurements. Thermal analysis revealed a significant depression of the melting point and, in certain cases, the degree of crystallinity of the polyacetal phase upon blending with the styrene-vinyl phenol copolymer.

INTRODUCTION

In an earlier paper, we reported that polyacetal, or poly(oxymethylene), is miscible in the amorphous phase with poly(vinyl phenol) [1]. Calorimetry-of-mixing studies performed on model compounds and analysis of melting point depression in the polymer blends indicated that the interaction driving miscibility was very strong, yielding a negative chi parameter on the order of unity in magnitude [1,2]. Applying our model compound calorimetry results quantitatively with a binary interaction model, we predicted that a random styrene/vinyl phenol copolymer containing as little as 10% vinyl phenol segments could exhibit miscibility with polyacetal.

The phase behavior of blends between homopolymers and copolymers has been well studied both experimentally and theoretically. In the cases where interactions are relatively weak and all components are amorphous, the binary interaction model, or modifications thereof, has been very successful at describing the phase behavior of blends providing that the segmental interaction parameter are known [3-6]. However, fewer studies have been performed on homopolymer/copolymer blend systems in which strong specific interactions are present or when crystallizable components are involved. Hydrogen bonding is known to strongly drive miscibility in certain homopolymer/copolymer systems. For example, styrene/vinyl phenol copolymers having as little as 2% vinyl phenol in the copolymer were found to be miscible with poly(methyl methacrylate) [7,8].

The present paper considers melt-blended mixtures of a semi-crystalline polymer, polyacetal, with a copolymer whose minority repeat unit, vinyl phenol, is capable of strongly interacting with the first polymer. The majority repeat unit, styrene, is non-interacting.

Evidence for miscibility will be presented and the results are rationalized in terms of hydrogen bonding interactions.

EXPERIMENTAL

The materials used in this study are described in Table 1. The polyacetal is an injection molding grade copolymer (Celcon M-90) obtained from Hoechst Celanese (^{13}C) NMR revealed its ethylene oxide content to be 2-3%. The styrene/vinyl phenol copolymer (S-VP) was also obtained from Hoechst Celanese. ^{1}H and ^{13}C NMR verified that its composition was 35 mol% VP (37 wt% VP).

The blends were prepared by melt compounding of pre-dried powder blends using a laboratory scale 15 mm Baker-Perkins co-rotating twin-screw extruder. A barrel temperature of 240°C and screw rotation speed of 300 RPM were maintained throughout. Compounded blends were compression molded at a temperature of 230°C.

Dynamic mechanical testing was performed using a Polymer Laboratories DMTA operating in the single cantilever beam mode at a frequency of 10 Hz and a heating rate of 3°C/min. Differential scanning calorimetry was performed using a Seiko RTC 220 using heating and cooling rates of 20 °C/min.

RESULTS AND DISCUSSION

The dynamic mechanical spectrum of the pure polyacetal constituent (PAc) is shown in Figure 1. As discussed in an earlier paper, we associate polyacetal's relatively weak beta transition at -6°C with the glass transition of the amorphous phase [1]. The pure styrene-vinyl

phenol copolymer (S-VP) was too brittle for dynamic mechanical analysis. However, DSC analysis clearly showed that the amorphous copolymer exhibits a glass transition at 125°C.

The dynamic mechanical spectra of two PAc/S-VP blends are shown in Figure 2. Figure 2A shows a blend containing 20% S-VP copolymer which exhibits a peak in the loss tangent centered around 88°C. figure 2B shows a blend containing 40% S-VP copolymer which exhibits a single peak at 109°C. The association of these peaks with the glass transition of the amorphous phase of the blend follows from the observation that they increase in magnitude and approach the Tg of pure S-VP as the copolymer content increases. Furthermore, the magnitude of the drop in storage modulus which is associated with this transition increases as the amount of copolymer in the blend increases.

Figure 3 plots the glass transition temperatures of the PAc/S-VP blends versus blend composition and compares these results to data reported previously for polyacetal blends with poly(vinyl phenol) homopolymer [1]. The plots are similar with the exception that the Tg values for the copolymer-containing blends are slightly lower than those of the homopolymer-containing blends to a degree that is consistent with the lower Tg of the copolymer compared to that of the vinyl phenol homopolymer. Thus, we conclude that both blend systems are miscible in the amorphous phase.

Differential scanning calorimetry was performed on the blends in order to examine the effect that the added copolymer exerts on the melting behavior of the crystalline polyacetal phase. In a previous paper, we showed that the melting point of polyacetal was depressed by blending with pol(vinyl phenol) homopolymer (PVP). The results for the present blend system, PAc/S-VP, are summarized in Table 2. Figure 4 demonstrates that,

as the copolymer content of the blend increases, both the melting point (upon heating) and the temperature of crystallization (upon cooling) are significantly depressed. This result is consistent with miscibility in the melt state.

The approximate crystallinity of the present blends was calculated based upon the measured enthalpies of melting, the blend compositions, and the reported heat-of-fusion of polyoxymethylene crystals (326 J/g) [9]. The crystallinity of the polyacetal component is given in Table 2. The crystallinity of the polyacetal component of the blend was less than that of the neat PAc central only when S-VP was the major component of the blend.

The observation of intermediate glass transition temperatures and melting point depression relative to the pure blend constituents clearly indicates miscibility in the present system. PVP homopolymer was previously shown to be miscible and strongly interactive with polyacetal, whereas polystyrene homopolymer is immiscible with polyacetal. We propose that miscibility in the present blends is driven to a lesser extent by the so-called "copolymer effect" (the repulsive interactions between styrene and vinyl phenol segments within the copolymer), and to a greater extent by strong hydrogen bonding interactions between phenol moieties in S-VP and ether units in PAc.

CONCLUSIONS

Blends containing a commercial grade polyacetal and a styrene-vinyl phenol copolymer containing 35 mol% vinyl phenol segments were prepared by melt compounding. Miscibility in the blends was evidenced by a single glass transition at temperatures which were dependent upon composition and intermediate between those of the pure blend constituents. Thermal

analysis revealed crystallinity in the blends. A significant depression of the melting point of the crystalline component as the amorphous copolymer content increased provided further indication of miscibility.

ACKNOWLEDGEMENTS

We are pleased to acknowledge R. P. Gingrich and L. J. Sikirica for experimental assistance, and G. W. Haddix for NMR analysis.

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9. B. Wunderlich, "Macromolecular Physics, Volume 3: Crystal Melting", Academic Press, New York (1980).

FIGURE CAPTIONS

Figure 1. Dynamic mechanical storage modulus, E′, and loss tangent, tan δ, as a function of temperature at a frequency of 10 Hz for the unblended polyacetal constituent.

Figure 2. Dynamic mechanical storage modulus ad loss tangent versus temperature at 10 Hz frequency for: a) an 80/20 PAc/S-VP blend; and b) a 60/40 PAc/S-VP blend.

Figure 3. Glass transition temperature as a function of blend composition for: a) PAc/PVP homopolymer blends and; b) PAc/S-VP copolymer blends.

Figure 4. Melting temperature upon heating, Tm, and crystallization temperature upon cooling at constant rate, Tc, as a function of blend composition for PAc/S-VP blends.

Table 1. Materials Used in This Study.

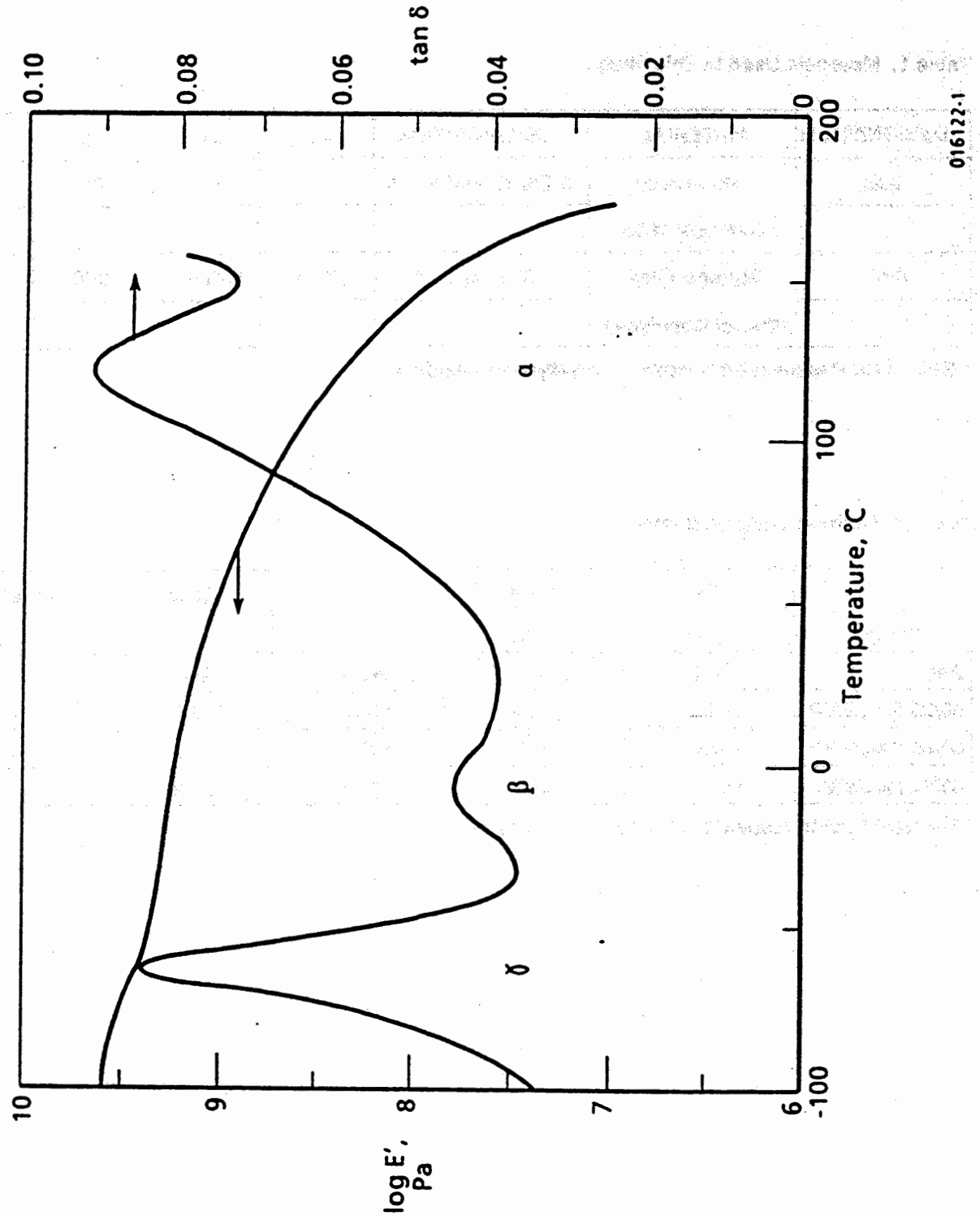
*DESIGNATION	MATERIAL	COMPOSITION	Mn*	Mw*	Tg	Tm
PAc	Polyacetal	2-3% Oxyethylene	-	-	-6°	170°C
	CELCON M-90					
S-VP	Styrene-Vinyl	35 mol% VP	37,200	80,900	125°C	-
	Phenol Copolymer					

* GPC in NMP expressed relative to polystyrene standards.

Table 2. Thermal Analysis Results

Sample	Tm (°C)	ΔHm (J/S)	Tc	ΔHc	Crystallinity* (%)
PAc	169.6	171.8	141.3	144.7	53
80/20 PAc/S-VP	166.3	138.6	139.7	123.9	53
60/40 PAc/S-VP	162.8	96.0	123.1	73.8	49
40/60 PAc/S-VP	154.1	52.4	72.8	23.2	40

*Normalized with respect to PAc content of blend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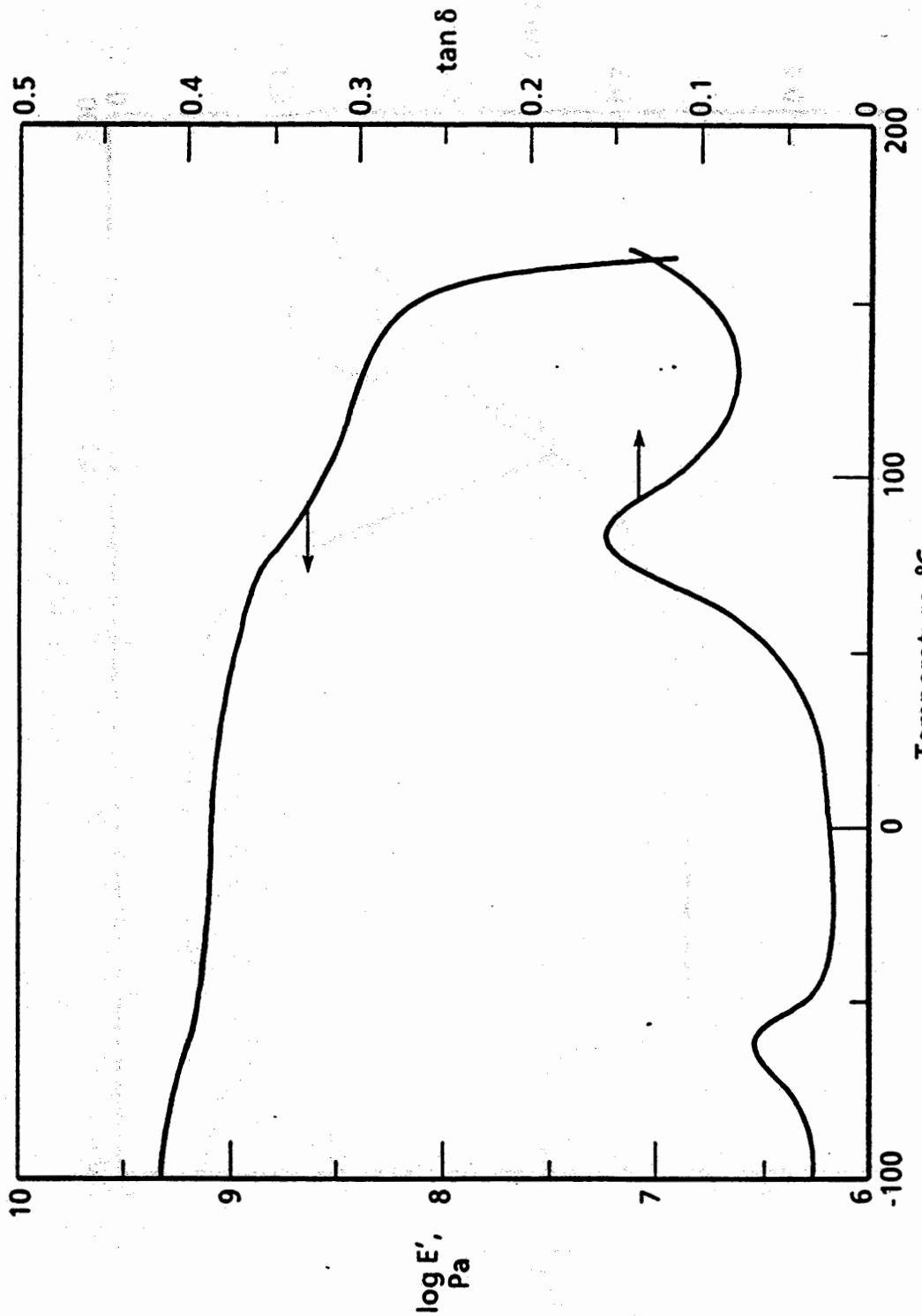
0.10
0.08
0.06
0.04
0.02
0
200
100
0
-100
Temperature, °C
log E', Pa
10
9
8
7
6
α
β
γ
016122-1

Fig 1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0.4
0.3
0.2
0.1
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100
0
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Temperature, °C
log E', Pa
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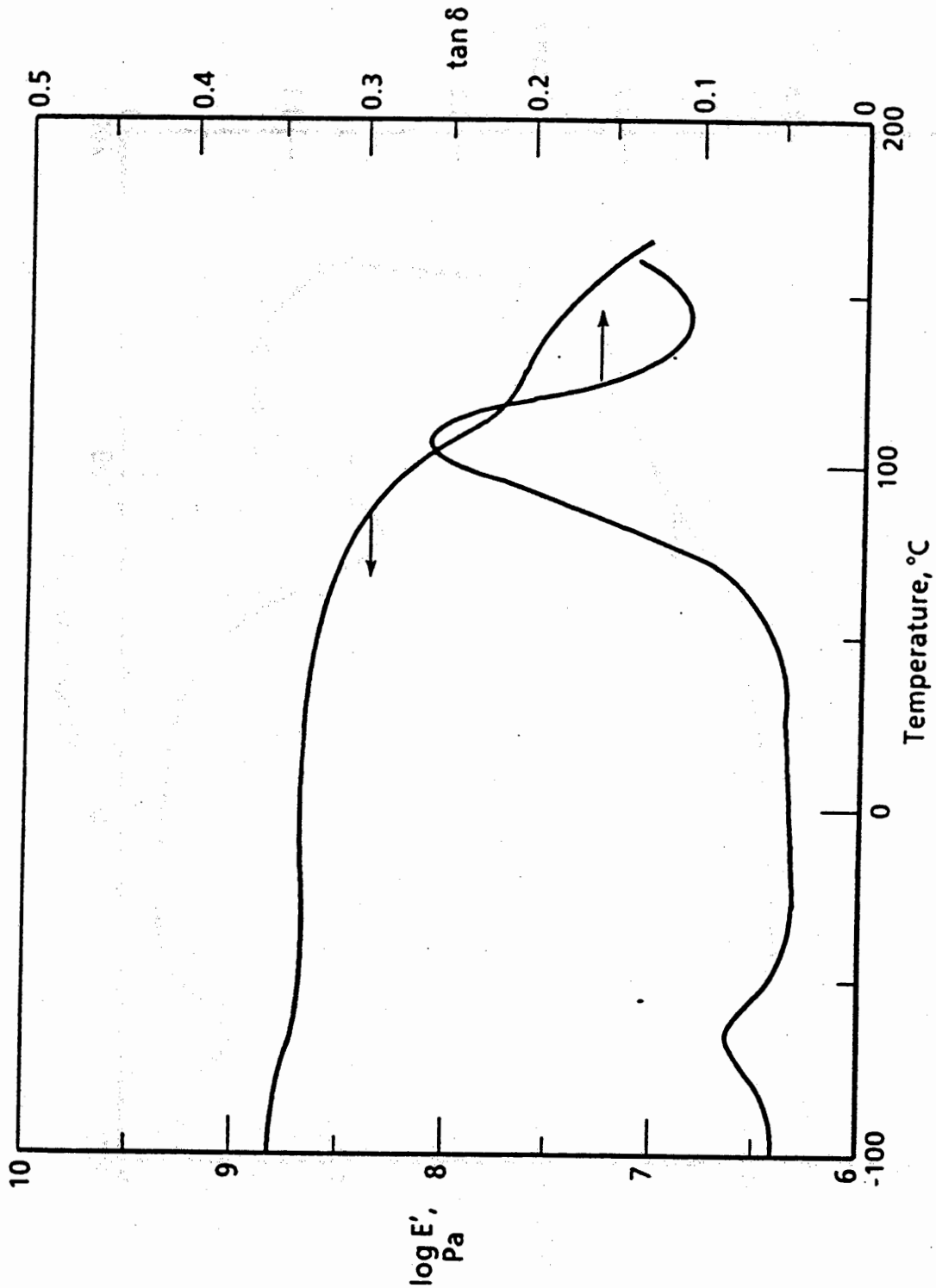
9
8
7
6
016122-2

Fig 29


tan δ
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0.2
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200
100
0
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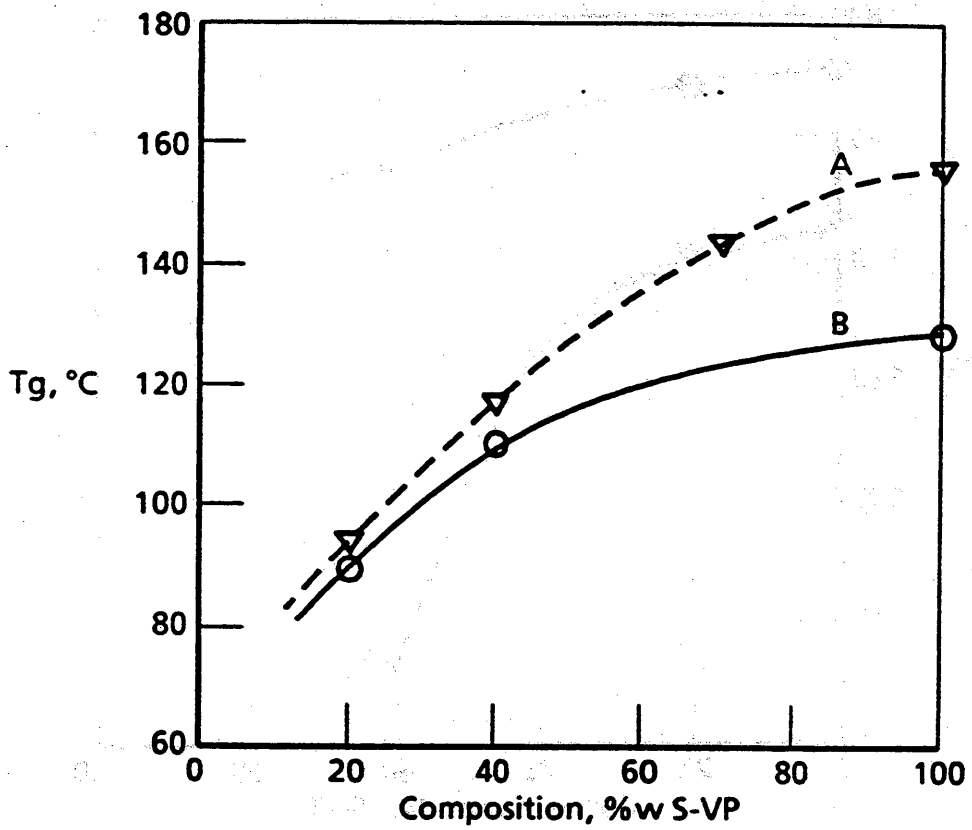
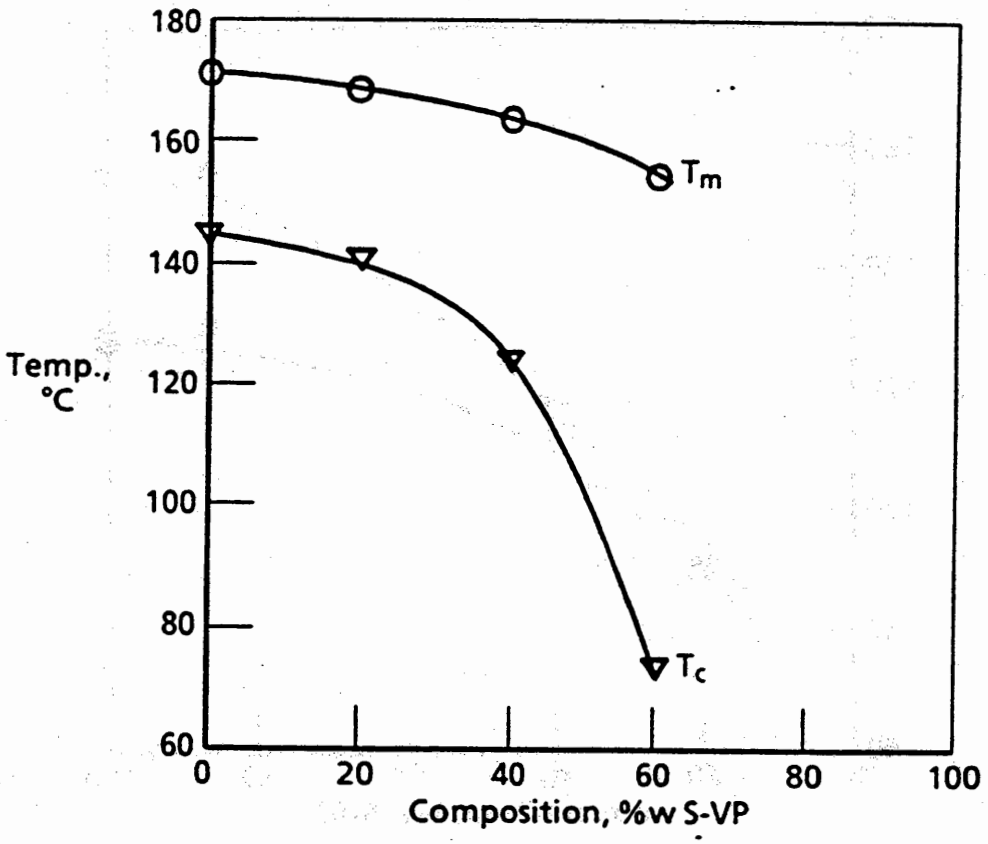
Temperature, °C
log E', Pa
10
9
8
7
6
016122-3

Fig 24


180
160
140
120
100
80
60
Tg, °C
A
B
0
20
40
60
80
100
Composition, %w S-VP

016122-4



016122-5

Fig 4

Appendix IV

Appendix 4

MAY 22, 1991 PROFS NOTE PAGE 1

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MONTHLY RESEARCH SUMMARY CONTRIBUTION

SUBMITTED FOR THE MONTH OF MAY,1991

PROJECT #	PROJECT TITLE	CATEGORY	R/C
62182	CARILON/TM/ POLYMER - APPLICATIONS	POLYMERS	SR

ARTICLE TITLE: POLYKETONE/POLYACETAL BLENDS CONTAINING A MUTUALLY MISCIBLE THIRD POLYMER

AUTHORS	DEPT	PROFS ID	AUTHORS	DEPT	PROFS ID
MACHADO, J. M.	730	MACHADO	LEE, C. S.	730	MACHADO

11 TOTAL REPORT PAGES INCLUDING ABSTRACT, TEXT, TABLES AND ILLUSTRATIONS

2 FIGURES (USE 0 IF THERE ARE NO FIGURES)

1 TABLES (USE 0 IF THERE ARE NO TABLES)

SECRETARY Doris Baskin RM C-2111 PHONE 8547 PROFS DDB19

CHECK IF APPLICABLE:

____ CAVEAT REQUIRED. (IT APPEARS ON TOP OF BOTH THE ABSTRACT AND FIRST PAGE OF THE ARTICLE).

Joseph M. Machado 5/22/91
AUTHOR(S) APPROVAL/DATE

JSB 5/31/91
MANAGEMENT APPROVAL/DATE MANAGEMENT APPROVAL/DATE

THANK YOU,
DORIS
PROFS: DDB19, ROOM C-2111, X8547

END OF NOTE

62182. CARILON® Polymer - Applications

Polyketone/Polyacetal Blends Containing a Mutually Miscible Third Polymer
J.M. Machado and C.S. Lee

Poly(vinyl phenol) is miscible in the melt and in the amorphous phase with both polyketone and with polyacetal. To some extent, poly(vinyl phenol) can perform as a compatibilizer for the immiscible polyketone/polyacetal blend system, yielding blends with improved tensile strength and finer domain size. However, the ductility and impact strength of these blends are rather poor.

62182. CARILON® Polymer - Applications

Polyketone/Polyacetal Blends Containing a Mutually Miscible Third Polymer

J.M. Machado and C.S. Lee

INTRODUCTION

CARILON® polymer and polyacetal are both semi-crystalline engineering thermoplastics with fairly similar property sets. Thus, the driving force to develop a compatible blend of these two polymers is not very great. Nevertheless, earlier blending studies have shown that poly(vinyl phenol) is miscible in the melt and in the amorphous phase with both of these polymers, suggesting that a strategy for compatibilization may be readily at hand [1,2].

The notion that the addition, to an immiscible polymer blend, of a third polymer which is miscible with both, improves compatibility might seem intuitively reasonable. Nevertheless, the mechanism by which compatibilization would occur is not altogether clear and this type of compatibilization is not well documented in the literature. Thus, the present case provides one opportunity to test this hypothesis and examine the efficiency of this compatibilization strategy. Therefore, in this work, we will look at poyketone/polyacetal blends and investigate the effect that adding minor quantities of poly(vinyl phenol) has upon the morphology and mechanical properties.

EXPERIMENTAL

The materials used in this study are CARILON® polymer P-1000/2, CELCON M-90 polyacetal copolymer, and poly(vinyl phenol) homopolymer obtained from Hoescht-Celanese with a Mw of 50,500 by GPC in NMP. Blends were melt compounded on a 30mm Haake co-rotating twin screw extruder. Specimens for mechanical testing were injection molded using an Arburg Allrounder and maintained in the "dry as molded" state prior to testing. Morphology was investigated by scanning transmission electron microscopy of RuO_4-stained sections which were microtomed from molded bars.

RESULTS AND DISCUSSION

Blends were prepared having polyketone/polyacetal ratios of 75/25, 50/50, and 25/75 and poly(vinyl phenol) contents of 0, 1, 3, and 10 pph. The poly(vinyl phenol) content is expressed per one hundred parts of PK/PAc blend so as to show that the PK/PAc ratio in the blend is held constant. The results of mechanical and notched Izod testing are given in Table 1.

Overall, the results demonstrate some level of compatibilization which unfortunately is partially masked by the deleterious effects that the "compatibilizer" has upon the two major blend components. For example, Table 1 shows that as PVP is blended with polyketone elongation at break and Izod impact strength decrease. Likewise, as PVP is blended with polyacetal, tensile strength, elongation, and notched Izod are all reduced significantly. However, as PVP is added to polyketone/polyacetal blends, properties are improved in some cases. For example, Table 1 shows that for 75/25 and 50/50 PK/PAc blends, tensile strength is improved by as much as

20% upon adding poly(vinyl phenol). Izod values are not improved, however.

Figure 1 demonstates this tendency towards compatibilization by plotting tensile strength versus PK/PAc ratio in the absence and presence of PVP. In the absence of PVP, the plot exhibits a concave shape which is characteristic of an incompatible blend. In the presence of PVP, the plot shows a convex shape which is characteristic of a compatible system.

Microscopy studies provide more evidence for compatibilization. Figure 2 shows micrographs of 50/50 PK/PAc blends with and without PVP. The addition of PVP results in a significant decrease in domain size consistent with compatibilization. This domain size reduction is somewhat less than what would be expected from an ideal block copolymer compatibilizer, however. The addition of the PVP also causes a qualitative change in the morphology, in which the dispersed polyacetal phase takes on a more skeletal structure giving the appearance of a bi-continuous morphology in the compatibilized blend.

CONCLUSIONS

There is some evidence, based on observation of tensile strength and blend morphology, that poly(vinyl phenol) is capable of compatibilizing polyketone/polyacetal blends. Unfortunately, the blends did not exhibit high levels of ductility and impact strength expected from a compatibilized system which can be rationalized in light of the extreme brittleness of poly(vinyl phenol) homopolymer.

REFERENCES

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2) D.L. Handlin, U.S. Patent 4,812,522.

Table 1. Mechanical properties of polyketone/polyacetal/poly(vinyl phenol) blends.

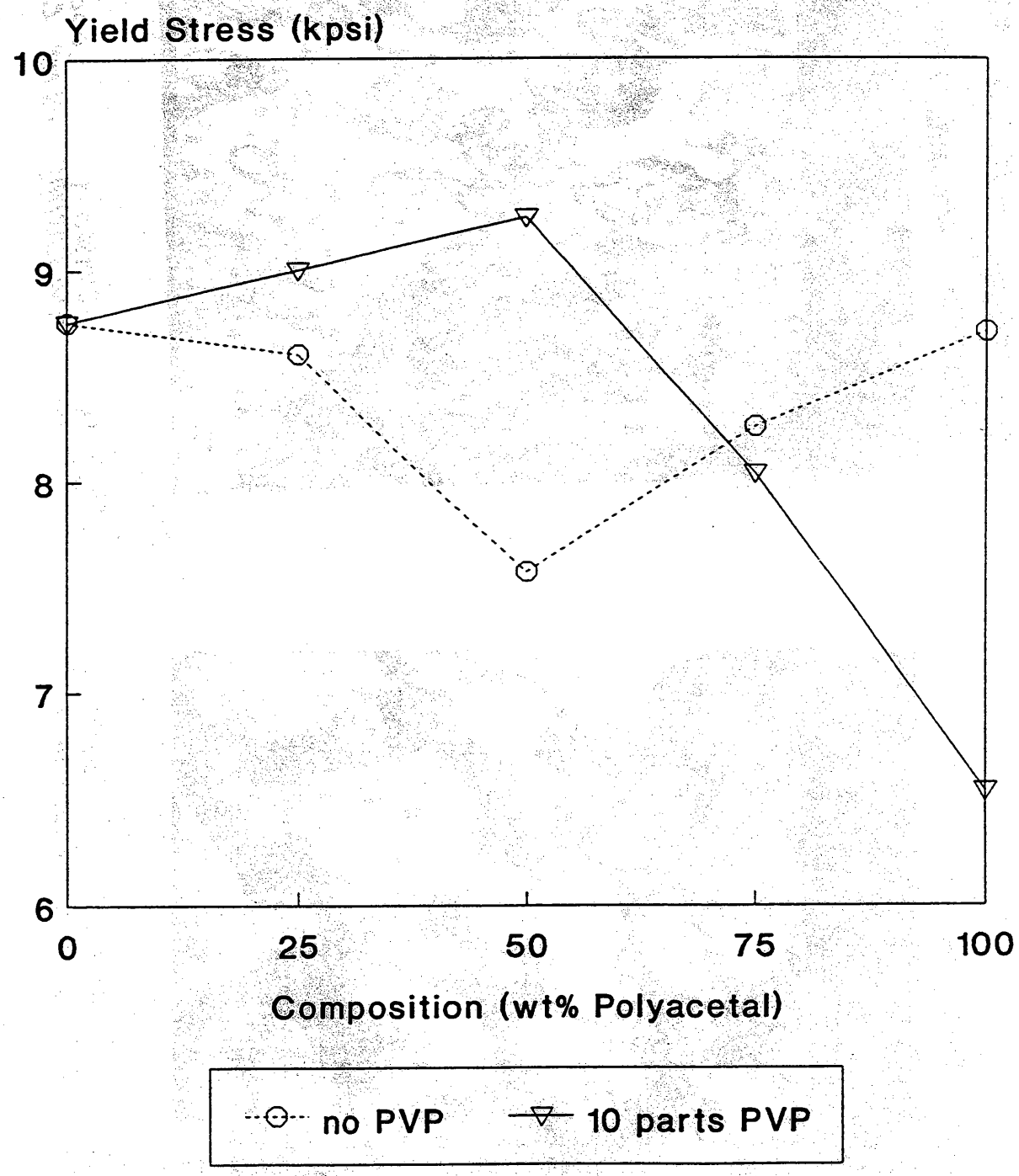
PK	PAc	PVP	Tensile Strength*	Elong.	Izod
(parts by weight)			(psi)	(%)	(ft-lb/in)
100	0	0	8750	329	5.2
100	0	10	8750	203	2.4
75	25	0	8600	94	3.0
75	25	3	8840	38	2.0
75	25	10	9002	100	1.8
50	50	0	7570	8	1.1
50	50	1	7720	10	1.1
50	50	3	7240	8	1.0
50	50	10	9250	10	0.6
25	75	0	8260	14	0.7
25	75	3	8130	8	0.6
25	75	10	8040	5	0.6
0	100	0	8710	25	1.3
0	100	10	6540	4	0.5

* for samples which yield, the yield stress is reported here

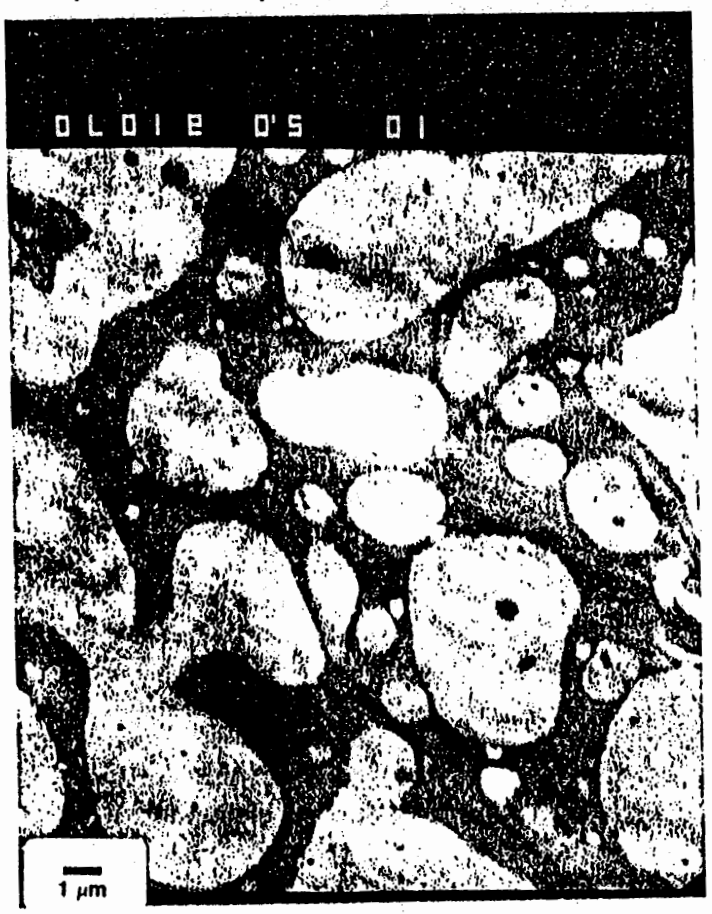
Figure Captions

Figure 1. Tensile strength versus polyketone/polyacetal ratio in the presence and absence of poly(vinyl phenol) compatibilizer.

Figure 2. STEM micrographs of 50/50 polyketone/polyacetal blends with and without 10 pph poly(vinyl phenol).


Yield Stress (kpsi)
10
9
8
7
6
0
25
50
75
100
Composition (wt% Polyacetal)
no PVP
10 parts PVP

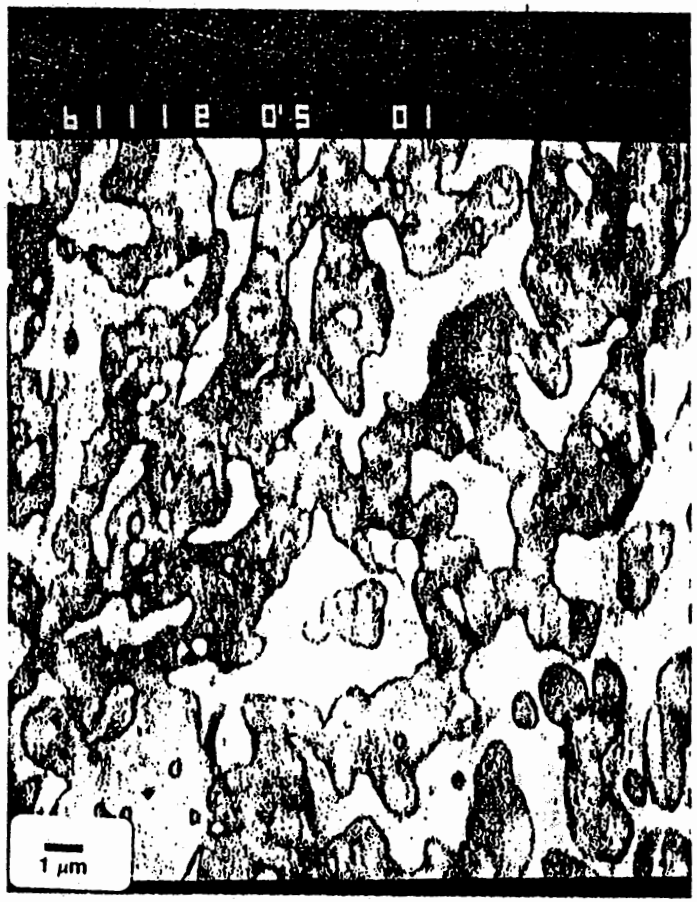
50/50 ~~CAR~~ PK / PAC



Machado 274860-1 5,000X
ML17-2 50/50 Car/PAC RuO_4 stained

50/50 PK/PAC + 10 parts PVP

~~45/45/10 CAR/PAC/PVP~~



Machado 274960-4 5,000X
ML17-2C 50/50 CAR/PAC 10% PVP RuO_4